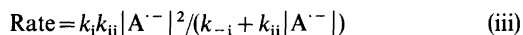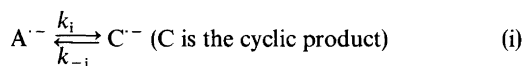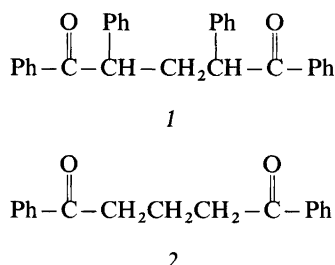# The Kinetics and Mechanism of the Cyclization of the Anion Radicals of 1,3-Dibenzoyl-1,3-diphenylpropane and 1,3-Dibenzoylpropane

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The kinetics of the cyclization of the anion radical of 1,3-dibenzoyl-1,3-diphenylpropane in aceto-nitrile were investigated by linear sweep volt-ammetry, normalized potential sweep voltammetry and derivative cyclic voltammetry. The results of all of the measurements, including determination of the activation energy, are consistent with a mechanism consisting of reversible (i) followed by essentially irreversible electron transfer (ii) giving rise to rate law (iii). The major product of the

$$A^{\cdot-} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} C^{\cdot-} \quad \text{(C is the cyclic product)} \qquad \text{(i)}$$

$$C^{\cdot-} + A^{\cdot-} \xrightarrow{k_{ii}} C^{2-} + A \qquad \text{(ii)}$$

$$\text{Rate} = k_i k_{ii} |A^{\cdot-}|^2 / (k_{-i} + k_{ii} |A^{\cdot-}|) \qquad \text{(iii)}$$

cyclization was observed to be an isomer of 1,2,3,5-tetraphenyl-1,2-cyclopentanediol. ^{1}H NMR analysis of the product indicated a *trans* configuration of the diol with adjacent phenyl groups being either *cis-cis* or *trans-trans*. The latter possibility was deemed most likely on steric grounds. Apparent first order kinetics were observed during the cyclization of the anion radical of 1,3-dibenzoyl-propane which is consistent with the same mecha-nism with the cyclization step (i) being rate-determining or with the disproportionation mech-anism as had previously been proposed.

As a part of our continuing program on the study of the dimerization[1−9] and cyclization[10−20] reac-tions of ion radicals, we have carried out studies on the reactions of the anion radicals of 1,3-dibenzoyl-1,3-diphenylpropane (*1*) and 1,3-dibenzoylpropane (*2*).

O Ph   Ph O
‖ | | ‖
Ph−C−CH−CH$_2$CH−C−Ph

1

O   O
‖   ‖
Ph−C−CH$_2$CH$_2$CH$_2$−C−Ph

2

The electrocyclization of *2* had previously been in-vestigated by Savéant and co-workers[21,22] by linear sweep voltammetry (LSV) and convolution potential sweep voltammetry (CPSV). On the basis of their studies they proposed a disproportionation mechanism, eqns. (1) to (3) with either the cycliza-tion or the protonation step being rate-determining. No evidence for the oxidation of the anion radical

$$2\,A^{\cdot-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{2-} + A \qquad (1)$$

$$A^{2-} \xrightarrow{k_2} C^{2-} \qquad (2)$$

$$C^{2-} + ROH \xrightarrow{k_3} \text{products} \qquad (3)$$

(A$^{\cdot-}$) could be detected using voltage sweep rates as high as 1,000 V/s.[21] We elected to investigate the reaction in more detail and in order to do this chose *1* as the substrate with the thought that the phenyl substituents in the 1,3-positions might crowd the transition state for the cyclization and thus moderate the rate of the reaction.
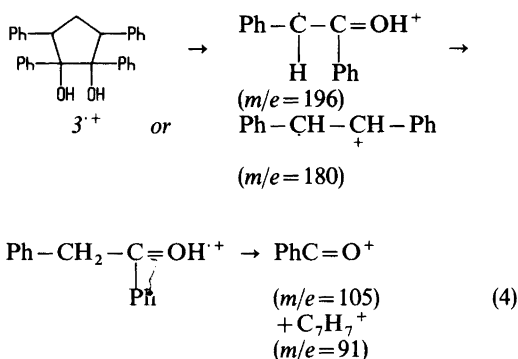
EXPERIMENTAL

Preparative scale electrolysis. A solution of *1* (1.01 g) in acetonitrile (100 ml) containing Me_4NBF_4 (0.07 M) was reduced at a platinum gauze electrode at a constant current of 50 mA (~ 1 mA/cm^2) over a period of 2.7 h (2 F/mol) in a divided cell under an atmosphere of nitrogen. After diluting with water and allowing to stand overnight, the crystals which had formed were gathered and recrystallized from methanol. More material was obtained by extraction of the solution with dichloromethane to give an isolated yield of about 50 %. No attempts were made to optimize the yield. The structure of the product was assigned on the basis of IR (no carbonyl absorption), mass and ^1H NMR (100 MHz) spectral data.

Kinetic studies. The instrumentation and data retrieval systems were the same as those recently described.[1] The working electrodes were constructed from platinum wire (0.4 mm) imbedded in glass and polished to a planar surface before electrolytically depositing mercury on the surface. The cells and reference electrodes were the same as previously described.[1] The temperature was controlled either by immersing the cell in an ice-water bath or with a Haake cryostat.

RESULTS

Structure of the isolated product. The mass spectral data are consistent with eqn. (4). The fragmentation pattern of the isolated product is


$$Ph-\underset{\underset{H}{|}}{C}-\underset{\underset{Ph}{|}}{C}=OH^+ \rightarrow$$

$(m/e = 196)$

$$Ph-\underset{+}{CH}-CH-Ph$$

$(m/e = 180)$

$$Ph-CH_2-\underset{\underset{Ph}{|}}{C}=OH^{\cdot+} \rightarrow PhC=O^+$$

$(m/e = 105)$ (4)
$+ C_7H_7^+$
$(m/e = 91)$

compared with that of the corresponding *cis*-diol prepared by reduction of *1* with amalgamated aluminum[29] in Table 7. All of the major ionic species are common to the two compounds. The double cleavage giving rise to the ions of mass 196 and 180 are of different proportions but of major importance in both spectra.

The ^1H NMR spectrum in CDCl$_3$ consisted of signals at δ 7.3 – 7.0 (20 H, m), 4.79 [2 H, t($J = 9$ Hz)], 2.85 [2 H, t($J = 9$ Hz)] and 1.84 (2 H, s). The singlet at 1.87 disappeared upon exposure to D$_2$O indicating exchange of hydroxyl H. There are three possible isomers with a *cis* arrangement of the hydroxyl groups. In structures *4* and *5* protons H$_a$ and H$_b$ are not equivalent as required by the

4   *5*   *6*
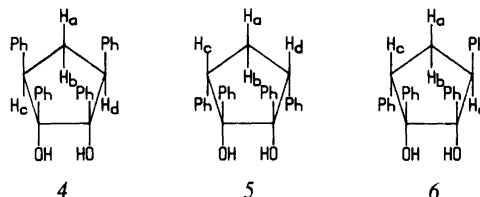
triplet at δ 2.85. Structure *6* is satisfactory with respect to H$_a$ and H$_b$ but in this case H$_c$ and H$_d$ are not equivalent as required by the triplet at δ 4.79. Thus, *trans* (with respect to the hydroxyl groups) isomers *7* and *8* remain as possibilities. This is also

7   *8*
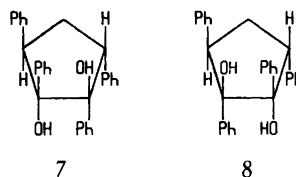
consistent with the fact that the spectrum of the product of amalgamated aluminum reduction of *1* was quite complex and did not contain the triplet at δ 4.79. That latter is at somewhat higher field than expected for benzylic protons and the reason for this is not clear. Protons H$_a$ and H$_b$ in the *cis* isomers give rise to signals close to δ 4.0. Molecular models suggest that there are considerable steric interactions between the *cis*-phenyl substituents in *7*. The transition state leading to cyclization of the intermediate giving rise to *8* would be of lower energy which suggests that *8* is the more likely structure of the isolated product.

LSV mechanism analysis. The data summarized in Table 1 can be analyzed according to eqns. (5) and (6)[23] in order to determine the reaction orders

$$dE^p/d \log v = [1/(b+1)]RT/nF \tag{5}$$

$$dE^p/d \log C_A = (a+b-1)/(b+1)RT/nF \tag{6}$$

Table 1. Linear voltammetry study of the cyclization reaction.[a]

C_A/mM	$dE^p/d \log v$[b]
2.00	21.1
1.00	22.4
1.00	21.8
1.00	21.1
0.500	20.2
$dE^p/d \log C_A$[c]	−16.4

[a] In acetonitrile containing Bu_4NBF_4 (0.1 M) at 0 °C. [b] In mV/decade from correlation of data with v ranging from 100 to 1000 mV/s. [c] In mV/decade from correlation of data measured at 1000 mV/s with C_A ranging from 0.50 to 2.00 mM.

Table 2. Normalized potential sweep voltammetry study of the cyclization reaction.[a]

v/mV s^{-1}	C_A/mM	NPSV slope[b]
973	0.53	1.060±0.012
96.1	0.53	0.979±0.005
973	1.01	1.046±0.004
96.1	1.01	0.954±0.004

[a] Measured in acetonitrile containing Bu_4NBF_4 (0.1 M) at 0 °C. [b] Analysis using theoretical data for the rate law, Rate $= k_{app}C_A^{2 \cdot -}$. The error limits are the standard deviations in 10 analyses.

in substrate (*a*) and anion radical (*b*). At 273.15 K, $(\ln 10)RT/F$ is equal to 54.17 mV. The mean value of $dE^p/d \log v$ in Table 1 is 21.3 ± 0.8 mV/decade. This implies a reaction order of 1.55 in the anion radical. The value required for a second order reaction is 18.1 mV/decade at this temperature. The fractional reaction order implies a complex rate law or competing mechanisms. If the reaction order *a* is 0, application of (6) with *b* equal to 1.55 results in a prediction of −14.9 mV/decade for $dE^p/d \log C_A$, somewhat lower than the observed value, −16.4. In order to be consistent, $dE^p/d \log v$ must differ from 18.1 by the same number as $dE^p/d \log C_A$ differs from −18.1. The values most consistent with the data are 20.6 and −15.6 mV/decade for the two slopes. These values are within experimental error of the observed values. Application of eqn. (5) using 20.6 mV/decade for $dE^p/ \log v$ results in a reaction order of 1.64 for the anion radical.

Normalized potential sweep voltammetry (NPSV) analysis. A direct comparison of experimental data with theoretical electrode potentials can be made by normalizing the current along the voltammetric wave by dividing by the peak current and expressing the potential relative to that where the current is half the peak value.[24] The theoretical data selected for the analysis corresponded to processes with rate law (7). NPSV data are summarized in Table 2. For a perfect data fit for

$$\text{Rate} = k_{app}C_B^{2} \qquad (7)$$

mechanism assignment, the NPSV slope is equal to unity. The data show that the slope is close to 1.0,

is somewhat dependent upon the sweep rate and is independent of the substrate concentration. The sweep rate dependence and the deviation from unity of the slope suggest that the rate law deviates from the simple second order case (7). That the deviations are not large suggests that the mechanism of the electrode process gives rise to a rate law similar to (7) but perhaps somewhat more complex. Thus, the NPSV analysis is consistent with the LSV data.

The disproportionation equilibrium constant. The observation of kinetics with a reaction order in anion radical greater than 1 suggests that disproportionation might be involved as was concluded for a related cyclization reaction.[21,22] Since both the anion radical and the dianion are very short-lived a direct measure of the potential difference for the first and second reduction stage needed to calculate the equilibrium constant for reaction (1) cannot be obtained by cyclic voltammetry. Phase selective second harmonic *a.c.* voltammetry[25] gives a reliable estimate of electrode potentials even in the case of very reactive systems.[26] The data summarized in Table 3 illustrate the determination of K_{disp}. The

Table 3. Phase selective second harmonic *a.c.* voltammetric determination of the disproportionation equilibrium constant.[a]

Frequency/Hz	$\Delta E°$/mV	K_{disp}
100	259.2±0.2	3.7×10^{-5}
300	261.9±0.1	3.4×10^{-5}
1,000	266.3±0.2	2.8×10^{-5}

[a] Measured in acetonitrile containing Bu_4NBF_4 (0.1 M). *D.c.* voltage sweep rate equal to 50 mV/s. The error limits are the standard deviations in six determinations.

Table 4. Derivative cyclic voltammetry reaction order analysis.[a]

C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_A$
1.00	170.2 ± 14.4	170.2
0.50	84.3 ± 7.7	168.6
0.50	82.1 ± 6.9	168.3

[a] Measured during the reduction of *1* in acetonitrile containing Bu$_4$NBF$_4$ (0.1 M) at 0 °C. The error limits are the standard deviations in 10 measurements.

fact that the potential difference is frequency dependent indicates that the value at the highest frequency is most reliable and that this will give a maximum estimate of K_{disp}, probably quite close to the real value.

Derivative cyclic voltammetric kinetic analysis. Direct electrode kinetic techniques such as cyclic voltammetry can also be used to obtain reaction orders.[27] In this case, it is not possible to separate a and b and the reaction order expressing the contributions of both A and B, $R_{A/B}$, is given by eqn. (8) where $v_{\frac{1}{2}}$ is the voltage sweep rate necessary for the ratio of the peak heights on the first derivative

$$R_{A/B} = 1 + z (v_{\frac{1}{2}}/C_A^z = \text{constant}) \tag{8}$$

of the reverse and forward scans of a cyclic voltammogram, R'_1, to be constant at 0.500 and z is the power to which C_A must be raised in order that $v_{\frac{1}{2}}/C_A^z$ be constant. Data for the reduction of *1* in acetonitrile are summarized in Table 4. The data indicate that z in this case is unity which results in $R_{A/B} = 2$. This reaction order is consistent with

rate law (7) but does not rule out rate law (9). However, we are unable to find a reasonable

$$\text{Rate} = k_{app} C_A C_B \tag{9}$$

mechanism for the cyclization reaction giving rise to (8). The LSV and NPSV analyses both indicate that a is zero and b closer to 2 than 1. The data in Table 4 are over a limited concentration range. The reason for this is that the high rate of reaction places an upper limit on the substrate concentration and poor reproducibility in the response, which gets severe at low concentrations, setting a lower limit at about 0.5 mV for meaningful measurements. That the system does not behave ideally is obvious from the standard deviations in $v_{\frac{1}{2}}$ of the order of 10 %. We normally find deviations of the order of ± 1 % for well behaved systems. A possible reason for the problems with reproducibility is suggested by the fact that it was necessary to renew the mercury surface frequently. This is normally not necessary and indicates that some species formed during the electrode process attack the surface.

Activation parameters for the cyclization. Data from two activation energy determinations are summarized in Table 5. Due to the problems mentioned in the previous section, several attempts to measure the activation parameters failed. The data reported in Table 5 were obtained by first making the measurements at 0 °C then at the other temperatures and finally the 0 °C measurement was repeated. If the two 0 °C measurements differed by more than 10 %, the data was considered unreliable. Two similar runs were discarded because of deviations as great as 50 %. The rate constants reported in the third column were cal-

Table 5. Rate constants and activation parameters for the cyclization reaction in acetonitrile.[a]

T/K	$v_{\frac{1}{2}}$/V s^{-1}	10^{-6} k/M^{-1} s^{-1}	
273.2	174.9	1.52	$E_a = 2.84$ kcal/mol
285.5	243.8	2.02	$k_{298} = 2.39 \times 10^6$ M^{-1} s^{-1}
294.8	274.2	2.20	$\Delta S_{298} = -29.3$ cal/K mol
273.2	176.9	1.53	$r = -0.986$
259.6	103.3	0.94	$E_a = 2.69$ kcal/mol
273.2	153.9	1.34	$k_{298} = 1.91 \times 10^6$ M^{-1} s^{-1}
285.1	185.2	1.54	$\Delta S_{298} = -29.8$ cal/K mol
296.2	226.9	1.82	$r = -0.989$
273.2	146.2	1.27	

[a] Measured during the reduction of *1* in solvent containing Bu$_4$NBF$_4$ (0.1 M) at a mercury electrode. The activation parameters on the right were calculated for the two separate runs.

culated from $v_{\frac{1}{2}}$ assuming rate law (7). The feature of most interest in the data is that the E_a values are much lower than expected for a bimolecular reaction with a rate constant of 2×10^6 M^{-1} s^{-1} at 298 K. In fact, the activation energy appears to be lower than expected for a diffusion-controlled reaction which is a clear indication of a complex mechanism.[28] The entropy of activation, -29 cal/K mol, is also somewhat larger than would be expected for a simple second order electron transfer reaction as in forward step (1).

Derivative cyclic voltammetric kinetic study of the cyclization of 1,3-dibenzoylpropane anion radical. Since the previous work on the reduction of *2* indicated that the mechanism of the cyclization was a disproportionation as in eqns. (1) to (3) with rate law (10) which differs significantly from that we find during the reduction of *1*, we reinvestigated

$$\text{Rate} = k_{\text{app}} C_B^2 / C_A \qquad (10)$$

the kinetics at a lower temperature where the reaction rate was low enough to be measured by cyclic voltammetry. Data measured at -26 °C are summarized in Table 6. As in the case of *1* the response was less reproducible than usual with variations of the order of ± 10 % in $v_{\frac{1}{2}}$. Within the limits of experimental error, $v_{\frac{1}{2}}$ was observed to be independent of the substrate concentration indicating apparent first order kinetics. The latter is consistent with previous work[21,22] and with rate law (10). However, the data do not rule out mechanism (11)–(12) with rate determining cyclization (11).*

DISCUSSION

The observation that kinetic data fit either rate law (7) or (10) can be taken as evidence for the
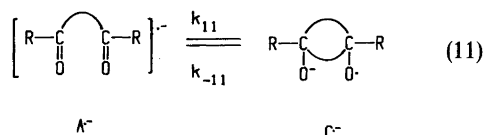
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* This mechanism was ruled out under the conditions of previous studies.[21,22]

Table 6. Kinetic data for the cyclization of the anion radical of 1,3-dibenzoylpropane in acetonitrile.[a]

C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	k_{app}/s^{-1}
0.50	353 ± 53	3.7×10^3
1.00	395 ± 8	4.2×10^3
2.00	367 ± 23	3.9×10^3

[a] Measured in solvent containing Bu$_4$NBF$_4$ (0.1 M) at a mercury electrode at -26 °C.

disproportionation mechanism (1) to (3) for the cyclization reactions of *1* and *2*. However, the evidence is not unambiguous. An alternative mechanism involving the cyclization of the anion radical in reversible reaction (11) followed by electron transfer reaction (12) and product-forming reaction (3) also gives rise to the same rate laws

$$\left[R-\overset{\text{O}}{\underset{\text{O}}{\text{C}}} \quad \overset{\text{O}}{\underset{\text{O}}{\text{C}}}-R \right]^{\cdot -} \quad \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} \quad R-\overset{\text{O}^-}{\text{C}} \quad \overset{\text{O}\cdot}{\text{C}}-R \qquad (11)$$

$$A^{\cdot -} \qquad\qquad\qquad C^{\cdot -}$$

$$A^{\cdot -} + C^{\cdot -} \xrightarrow{k_{12}} C^{2-} + A \qquad (12)$$

depending upon whether (12) or (3) is rate-determining. However, if (11) cannot be considered to be in equilibrium the rate law is more complex and the reaction order in A$^{\cdot -}$ would be expected to be less than 2 as is evident from (13).

$$\text{Rate} = k_{12} k_{11} |A^{\cdot -}|^2 / (k_{-11} + k_{12} |A^{\cdot -}|). \qquad (13)$$

The fact that the apparent activation energy for the cyclization of $1^{\cdot -}$ is less than 3 kcal/mol under conditions where the observed second order rate constant is of the order of 10^6 M^{-1} s^{-1} is a very clear indication that the reaction does not involve rate-determining disproportionation reaction (1). The value of E_a observed is even too low for a diffusion-controlled reaction. On the other hand, mechanism (11)–(12) readily accounts for the low E_a. It is probable that equilibrium (11) would be shifted to the right by lowering the temperature. Thus, this inverse temperature effect on (11) would

Table 7. Mass spectral data from the electrolytic and amalgamated aluminum reduction products.[a]

	Relative abundance	
m/e	Electrolytic	Amalgamated aluminum
406	18.5	17.6
196	100	95.8
180	42.1	100
105	97.8	97.1
91	20.0	21.2
77	45.5	38.6

[a] Reduction products of *1*.

counteract that on (12) and result in an apparently anomolous E_a.

Rate law (13) is consistent with the LSV results as well. Under the conditions of the LSV study, the reaction order in $A^{\cdot-}$ is clearly less than 2. It was also pointed out that the NPSV results suggest a rate law more complex than (7). Other than the low E_a obtained by derivative cyclic voltammetry, the latter technique did not reveal the complex rate law. Complex reactions sometimes do appear more simple as has been amply demonstrated in related work.[28] Thus, the fact that the reaction appears to be second order under some conditions cannot be considered as evidence against mechanism (11)–(12). This mechanism can give reaction orders in $A^{\cdot-}$ ranging from 1 to 2, depending upon the relative magnitudes of the terms in the denominator of (13).

The disproportionation equilibrium constant calculated from the second harmonic *a.c.* measurements, $<2.8\times10^{-5}$, can be used to estimate the maximum possible second order rate constant for forward reaction (1). If the back reaction (1) is assumed to be diffusion-controlled, $k_{-1}\sim10^{10}$ M^{-1} s^{-1}, the maximum value of k_1 consistent with the data is $<2.8\times10^5$ M^{-1} s^{-1}. The value of k_{298} obtained from the Arrhenius correlation, Table 5, is about an order of magnitude greater. While this is not compelling evidence because of the approximations made in the estimate it does add further support to the arguments based on the other kinetic data.

The reactions of $2^{\cdot-}$, as can be seen from the data in Table 6, are so rapid that an activation energy determination was not attempted. Thus, we have no evidence in this case that the reaction does not follow a simple disproportionation. On the other hand, mechanism (11)–(12) cannot be ruled out. In fact, it seems highly unlikely that the structural change in going from $1^{\cdot-}$ to $2^{\cdot-}$ would cause a change in the mechanism of cyclization. Equilibrium (11) would be expected to be even more favorable for $2^{\cdot-}$ and would be more rapid because of the unfavorable steric interactions for the reactions of $1^{\cdot-}$. We therefore conclude that (11)–(12) represents the most likely mechanism for both anion radicals.

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