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Mechanisms of the Electrohydrodimerization of Activated Olefins. VI.* Cyclohydrodimerization of *p*-Methylbenzylidene Malononitrile Anion Radical

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The kinetic and activation parameters were obtained for the electrocyclohydrodimerization of *p*-methylbenzylidene malononitrile (MBM) anion radical in acetonitrile (AN), *N*,*N*-dimethylformamide (DMF) and in AN containing acetic acid. In solution in the absence of acid, hydrodimerization is accompanied by the formation of base which reacts with substrate giving rise to complex kinetic behaviour. In the presence of acetic acid the proton donor does not become involved until after the dimer forming reactions and the kinetics are simplified. Under conditions where the electrogenerated base does not influence the kinetics, rate law (i) is followed. Activation energies at low substrate concentration

$$\text{Rate} = k_{\text{app}}|\text{MBM}^{\cdot-}|^2 \qquad \text{(i)}$$

were observed to be 0.94 (AN) and 1.6 (DMF) kcal/mol with corresponding entropies of activation equal to −25 and −28 cal/K mol, respectively. The mechanism is proposed to involve a reversible dimerization of anion radicals followed by protonation of the dimeric dianion and cyclization of the resulting carbanion. The evidence is examined with relation to previous reports of the electrohydrodimerization of MBM.

The question of the mechanism of the electrohydrodimerization (EHD) of activated olefins has been reopened after nearly a decade of acceptance of the anion radical dimerization (1) as the key step

$$2\text{R}^{\cdot-} \rightarrow \text{R}^- - \text{R}^- \qquad (1)$$

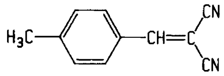
in the mechanism by most workers in the field.[1–5] The literature in this area was surveyed in another part of this series.[3] The recent work [1–5] has demonstrated that the anion radical–substrate coupling mechanism (2)–(3) can play an important and in

$$\text{R}^{\cdot-} + \text{R} \rightarrow \text{R}^- - \text{R}^{\cdot} \qquad (2)$$

$$\text{R}^- - \text{R}^{\cdot} + \text{R}^{\cdot-} \rightarrow \text{R}^- - \text{R}^- + \text{R} \qquad (3)$$

some cases a predominant role in the overall reaction.

Reports of the electrohydrodimerization of *p*-methylbenzylidene malononitrile (*1*) has attracted our attention.[6–8] The reaction was first studied by linear sweep voltammetry (LSV) and convolution potential sweep voltammetry in acetonitrile at millimolar concentrations.[6,7] Excellent fits of the experimental to theoretical data for the anion radical dimerization (1) was found.[6,7] The peak potential during LSV was observed to be dependent upon the water concentration but the changes were related to those of the reversible potential which indicates that water is not kinetically involved in the reaction. The reaction was later studied by chronopotentiometry at high concentrations in order to test for a change in mechanism with increasing concentration.[8] The conclusion of this study was that the



1 = MBM

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* See Refs. 1–5 for other parts in this series.

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reaction remained of the anion radical dimerization type but that water playned a significant role when the concentrations of MBM$^{\cdot-}$ were increased. The effect of water was rationalized as follows; When the concentrations of MBM and water are of the same order of magnitude, the preferential solvation of the anion radical, A$^{\cdot-}$, by water was considered essentially as the formation of an adduct and the reactions rationalized as (4)–(7) where TH is water, AS$^{\cdot-}$ is the anion radical–water adduct, and D^{2-} is the dimer dianion. It was concluded that since coulombic repulsions are reduced in AS$^{\cdot-}$,

$$A^{\cdot-} + TH \overset{K_4}{\rightleftarrows} AS^{\cdot-} \tag{4}$$

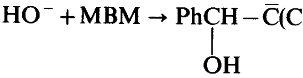
$$2AS^{\cdot-} \xrightarrow{k_5} DH_2 + 2T^- \tag{5}$$

$$AS^{\cdot-} + A^{\cdot-} \xrightarrow{k_6} DH^- + T^- \tag{6}$$

$$2A^{\cdot-} \xrightarrow{k_7} D^{2-} \tag{7}$$

the dimerization (5) can be considered to play a major role in the overall reaction.

We find the proposals by Nadjo and Savéant[8] concerning the mechanism of the electrohydrodimerization of MBM unacceptable from a number of considerations. (i) The fact that base is generated (T$^-$) was taken into account but the fact that MBM is readily attacked by hydroxide ion, as in (8), was neglected. A similar reaction has been shown[3]

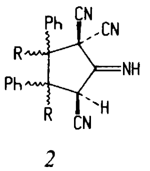


$$HO^- + MBM \rightarrow \underset{\displaystyle OH}{PhCH} - \bar{C}(CN)_2 \tag{8}$$

to be responsible for the low coulometric n values observed during electrohydrodimerization of diethylfumarate.[9]

(ii) If equilibrium (4) is important at high MBM concentrations it should also be important when MBM is in the millimolar range and the water concentration is increased. This was not observed.

(iii) Work by Avaca and Utley has shown that the product of hydrodimerization of MBM in DMF containing acetic acid is not the normal hydrodimer as assumed by Savéant and co-workers[6–8] but rather the cyclic structures (*2*) and (*3*).[10–11]



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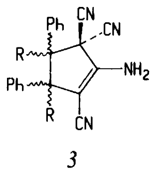

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The points raised in the previous paragraph prompted us to undertake a reinvestigation of the electrohydrodimerization of MBM in order to more clearly define the effect of proton donors, to find the effect of base on the overall reaction pathway and to compare the mechanisms in the two solvents previously used, AN[6,7] and DMF.[8,10,11]

RESULTS

Kinetic method. We found that the kinetics of the dimer forming reactions of MBM$^{\cdot-}$ could be studied by derivative cyclic voltammetry (DCV)[12,13] in both AN and DMF. The data were treated by the reaction order approach recently described.[14] The essential feature of the method is embodied in eqns. (9) and (10). The reaction order $R_{A/B}$ refers to the sum of the order in substrate (A) and intermediate (B) reacting in process (11). The quantity z is the power to which C_A must be raised in order for relationship (10) to hold where $v_{\frac{1}{2}}$ is the voltage sweep rate necessary for the derivative peak ratio to equal 0.500. For the simple dimerization mechanism (1) the reaction order in substrate is 0 and that in the intermediate anion radical is 2 which results in $R_{A/B}=2$ and $z=1$. On the other hand, the anion radical–substrate coupling mechanism (2)–(3) follows rate law (12) which corresponds to $R_{A/B}=3$ and $z=2$. Further detail and discussion of the method can be found in Ref. 14.

$$R_{A/B} = 1 + z \tag{9}$$

$$v_{\frac{1}{2}}/C_A^{z} = \text{constant} \tag{10}$$

$$A \pm e^- \rightleftarrows B \rightarrow \text{products} \tag{11}$$

$$\text{Rate} = k_{app}|R^{\cdot-}|^2|R| \tag{12}$$

The kinetics in acetonitrile. Data for two series of measurements carried out in AN at −39.8 °C are summarized in Table 1. The reaction was observed to be quite rapid and required the use of high v. The column headed $v_{\frac{1}{2}}/C_A$ ahows the test for the dimerization of anion radicals (1) which is characterized by $z=1$ and $R_{A/B}=2$. Adherence to this mechanism requires that $v_{\frac{1}{2}}/C_A$ remains constant while C_A is varied. The data show a decreasing trend as C_A was increased. The next two columns test $z=0.75$ and $z=0.5$. The values of $v_{\frac{1}{2}}/C_A^{z}$ were averaged

Table 1. Reaction order analysis of the electrohydrodimerization of MBM in acetonitrile.[a]

C_A/mM	$\|H_2O\|^b$/M	$v_{1/2}$/V s^{-1}	$v_{1/2}/C_A$	$v_{1/2}/C_A^{0.75}$	$v_{1/2}/C_A^{0.5}$
0.25	0	165	660	466	330
0.50	0	250	500	420	354
1.00	0	440	440	440	440
			533(114)	442(23)	375(58)
0.25	0.1	160	640	452	320
0.50	0.1	250	500	420	354

[a] Data measured in solvent containing Bu_4NBF_4 (0.1 M) at a mercury electrode at −39.8 °C. [b] Refers to the concentration of added water.

Table 2. Reaction order analysis of the electrohydrodimerization of MBM in DMF.[a]

C_A/mM	$v_{1/2}$/V s^{-1}	$v_{1/2}/C_A$	% Deviation[b]
0.10	14.8	148	6.9
0.20	32.2	161	1.3
0.30	48.1	160	0.6
0.50	77.6	155	2.5
0.70	118	169	6.3
1.00	166	166	4.4
2.00	304	152	4.4

[a] Measurements in solvent containing Bu_4NBF_4 (0.1 M), H_2O (0.2 M) at 298 K at a mercury electrode. [b] The percent deviation from the mean value.

for the first set of experiments. The standard deviations, in parentheses, are a measure of the best fit to eqn. (10). In this case, the best fit is clearly with $z=0.75$. Nearly identical results were obtained for the reaction in the presence of water (0.1 M) and the data for the two concentrations give a best fit to relationship (10) when z is midway between 0.5 and 0.75. The data indicate significant deviations from $R_{A/B}=2$ required for the simple irreversible dimerization of anion radicals (1).

The kinetics in DMF. The rate of the reaction of $MBM^{\cdot -}$ was observed to be considerably lower in DMF than in AN under comparable conditions. Data from measurements at 25 °C are summarized in Table 2. In this case, little deviation was observed

Table 3. The effect of water on the rate of electrohydrodimerization of MBM in AN and DMF.[a]

Solvent	T/K	$\|H_2O\|$/mM[b]	$v_c^c/V\,s^{-1}$	% Deviation[d]
AN	255	0	159	2.5
AN	255	100	167	
AN	255	200	162	
DMF	255	0	129	2.6
DMF	255	100	135	
DMF	255	200	135	
DMF	273	0	194	3.2
DMF	273	100	200	
DMF	273	200	207	
DMF	285	0	81.6	9.4
DMF	285	50	91.6	
DMF	285	100	99.5	
DMF	285	200	100.4	

[a] Measurements in solvent containing Bu_4NBF_4 at a mercury electrode. $E_{switch}-E_{rev}=500$ mV. [b] Water added to the solutions. [c] In AN c refers to 0.3 and in DMF to 0.5. [d] Percent deviation from the mean value in each set.

Table 4. Reaction order analysis of the electrohydrodimerization of MBM in AN containing acetic acid.[a]

C_A/mM	T/°C	|HOAc|/mM	$v_{0.3}$/V s^{-1}	$v_{0.3}/C_A$	% Dev.[b]
0.25	12	22	42.8	171.2	5.3
0.50	12	22	92.4	184.8	2.3
0.75	12	22	138.0	184.0	1.8
1.00	12	22	182.7	182.7	1.1
0.50	−26	0	88.9	177.8	3.9
0.50	−26	4.4	86.3	172.6	6.8
0.50	−26	8.8	97.5	195.0	5.3
0.50	−26	22	98.0	196.0	5.9
0.50	−26	44	92.0	184.0	0.6

[a] In solvent containing Bu_4NBF_4 (0.1 M) and water (0.1 M). [b] Percent deviation from the mean value.

in $v_{\frac{1}{2}}/C_A$ over a 20-fold C_A range. The data indicate that $R_{A/B}$ is 2 and that the kinetics are consistent with the irreversible dimerization reaction (1).

Tests for effect of water on the kinetics. Several series of experiments were carried out at constant C_A while the concentration of water was varied from 0 to 200 mM. The last column in Table 3 shows the standard deviations in each series expressed in percent of the mean value. Measurements at 255 K in either AN or DMF showed no dependence of the apparent rate constant on the water concentration. In DMF at 273 and 285 K, a small but definite increase of $v_{\frac{1}{2}}$ with increasing water concentration was apparent.

Kinetic analysis of reactions carried out in the presence of acetic acid. In the presence of HOAc (22 mM) in AN, $R_{A/B}$ was observed to be 2 as is evident from the small deviations in $v_{\frac{1}{2}}/C_A$ listed in the last column of Table 4. The quantity measured was $v_{0.3}$ which required considerably lower sweep rates and allowed the analysis to be carried out at higher temperature. The subscript 0.3 refers to a derivative peak ratio of 0.300. The set of experiments carried out at $C_A = 0.5$ mM summarized in the lower half of the table show that the apparent rate constant is essentially independent of the acetic acid concentration in the range, 0 to 44 mM. The deviations from the mean shown in the last column indicate that the

Table 5. Reaction order analysis of the electrohydrodimerization of MBM in DMF containing acetic acid.[a]

C_A/mM	|HOAc|/mM	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_A$	$v_{\frac{1}{2}}/C_A^{0.75}$
0.25	22.0	18.8	75.4	53.3
0.50	22.0	51.1	102.3	86.0
0.75	22.0	75.7	100.9	93.9
1.00	22.0	93.8	93.8	93.8
1.50	22.0	111.6	74.4	82.3
0.50	0	56.3	–	–
0.50	4.4	61.4	–	–
0.50	8.7	61.2	–	–
0.50	13.1	59.0	–	–
0.50	21.9	57.0	–	–
0.50	43.7	57.6	115.2	96.8
0.75	43.7	78.7	105.0	97.7
1.00	43.7	94.5	94.5	94.5
1.50	43.7	112.3	74.9	82.9

[a] In solvent containing Bu_4NBF_4 (0.1 M) and water (278 mM) at 11.5 °C.

apparent rate constant varied by about ±5 % in the series of measurements.

Data obtained for the EHD of MBM in DMF containing acetic acid are summarized in Table 5. In this case either at |HOAc| equal to 22 or to 44 mM, $v_{\frac{1}{2}}/C_A{}^{0.75}$ gave the best fit to relationship (10) indicating that $R_{A/B}$ is about 1.75. On the other hand experiments carried out at constant C_A (0.5 mM) indicate that the apparent rate constant is independent of the acetic acid concentration.

The effect of temperature on the apparent rate constants for the EHD of MBM. Since most of the data discussed so far indicate that the kinetic behaviour of the reaction approximates the simple dimerization of anion radicals (1) this mechanism was taken as the basis for the calculation of rate constants in order to evaluate apparent activation parameters. Rate constants can be evaluated from theoretical data using eqn. (13).[13] The constants c and m are dependent upon the mechanism and the difference between the switching and reversible potentials, $E_{sw}-E_{rev}$, and R'_I is the derivative peak ratio. The appropriate values of c and m can be obtained from Ref. 13. For the simple dimerization mechanism (1) with $R'_I=0.500$ and $E_{sw}-E_{rev}=$ 300 mV eqn. (13) reduces to (14).

$$k=(F/R)\,(v/C_A^zT)\exp\left[(\ln R'_I-c)/m)\right] \qquad (13)$$

$$k=1362\,v_{\frac{1}{2}}/C_AT \qquad (14)$$

The results of two sets of experiments on the EHD of MBM in AN are summarized in Table 6. In the first set of measurements C_A was 0.25 mM. The last column in the table gives rate constants calculated from the Arrhenius correlation of the experimental values listed in the previous column. The deviations from the experimental values were in all cases quite small. The second set of experiments were at C_A equal to 0.50 mM and |HOAc| was 22 mM. Once again, a very close correspondence was observed between the experimental rate constants and those obtained from the Arrhenius correlation.

Three sets of data for the temperature dependence of the apparent rate constant for the EHD reaction in DMF are summarized in Table 7. Data were obtained at C_A equal to 0.50, 1.00 and 4.00 mM and in all cases the correlations were very good.

Correlation coefficients for all of the data in Tables 6 and 7 were greater than 0.99. We find the comparison of the experimental values with those obtained from the correlation more instructive than the correlation coefficients.

The activation parameters obtained from the Arrhenius correlations of the data in Tables 6 and 7 are summarized in Table 8. The most striking features of the data are the low activation energies,

Table 6. The effect of temperature on the apparent second order rate constants for the electrohydrodimerization of MBM in AN.[a]

|HOAc|/mM	T/K	$v_c{}^b$/V s^{-1}	$10^{-6}k_{app}$/M^{-1}s^{-1}	$10^{-6}k_{corr}{}^c$
$C_A=0.25$ mM				
0	234	170	6.88	6.99
0	240	190	7.49	7.35
0	246	200	7.70	7.71
0	253	215	8.05	8.13
0	260	240	8.74	8.55
0	271	260	9.09	9.21
$C_A=0.50$ mM				
22	261.2	70.5	3.88	3.92
22	266.2	75.6	4.09	4.10
22	271.7	82.9	4.39	4.32
22	277.2	88.0	4.57	4.53
22	283.2	93.9	4.77	4.77
22	288.7	99.0	4.93	4.99

[a] In solvent containing Bu_4NBF_4 (0.1 M) and H_2O (0.1 M) at a mercury electrode. $E_{switch}-E_{rev}=300$ mV. [b] At $C_A=0.25$ mM c refers to 0.5 and $E_{sw}-E_{rev}=200$ mV while at C_A equal 0.50 mM, c refers to 0.3 and $E_{sw}-E_{rev}$ was 300 mV. [c] The apparent rate constant obtained from the Arrhenius correlation lines.

Table 7. The effect of temperature on the apparent second order rate constants for the hydrodimerization of MBM in DMF.[a]

T/K	$v_{\frac{1}{2}}$/V s^{-1}	$10^{-5}k_{\mathrm{app}}{}^{b}$/M^{-1}s^{-1}	$10^{-5}k_{\mathrm{corr}}{}^{c}$/M^{-1}s^{-1}
$C_A = 0.50$ mM			
257	40.5	4.29	4.38
262	45.7	4.75	4.66
268	49.1	4.99	4.99
273	53.2	5.31	5.27
279	58.1	5.67	5.62
287	63.3	6.01	6.09
$C_A = 1.00$ mM			
268.2	23.3	1.18	1.20
274.7	30.5	1.51	1.47
282.7	38.6	1.86	1.88
$C_A = 4.00$ mM			
263.2	67.6	0.875	0.864
268.2	80.6	1.02	1.04
274.7	107.0	1.33	1.32

[a] In solvent containing Bu_4NBF_4 (0.1 M) and water (0.2 M) at a mercury electrode. [b] Calculated from theoretical data assuming an EC(dim) mechanism as described in the text. [c] Calculated from the Arrhenius correlation.

ranging from 1 to 5 kcal/mol and the clear dependence of the value of E_a in both solvents upon the substrate concentration. This is a clear indication that the reactions are more complex than implied by the simple irreversible dimerization (1). It is also of interest to note that the apparent rate constants are significantly greater in AN and that the latter are lower in the presence of HOAc. The value of k_{298} in DMF when C_A was 0.50 mM appears to be larger by a factor of about 2 than expected from the other values obtained at higher C_A. The reason for this discrepancy is not clear. The series of measurements were repeated with nearly identical results.

LSV analysis of the EHD of MBM in acetonitrile. The dependence of the LSV peak potential on v and C_A can be analyzed by means of eqns. (15) and (16).[15] The lower case letters refer to reaction orders in A (a), B (b) and I (i), a species generated during the process which further participates. For the EC(dim) mechanism (1), dE^p/d log v is predicted by (15) to

$$\mathrm{d}E^p/\mathrm{d}\log v = [\ln 10/(b+1)]RT/nF \qquad (15)$$

$$\mathrm{d}E^p/\mathrm{d}\log C_A = [(a+b+i-1)\ln 10/(b+1)]RT/nF \qquad (16)$$

equal (ln 10) $RT/3F$ and eqn. (16) results in a number of the same magnitude for dE^p/d log C_A if both a and i are 0. Data along with the theoretical values for the EC(dim) mechanism for measurements in AN

Table 8. Activation parameters for the electrohydrodimerization of MBM.[a]

Solvent	C_A	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$/cal K^{-1} mol^{-1}	$k_{298}10^{-5}$/M^{-1} s^{-1}
AN	0.25	0.94	−25	108
AN (HOAc)[b]	0.50	1.3	−25	63.6
DMF	0.50	1.6	−28	6.8
DMF	1.00	4.7	−20	2.9
DMF	4.00	5.3	−18	2.8

[a] Data from Tables 6 and 7. The entropies of activation were calculated assuming that the frequency factor can be equated to kT/h exp($\Delta S/R$) and that ln k varies linearly with $1/T$. [b] 22 mM.

Table 9. Linear sweep voltammetry peak potential dependence on substrate concentration and voltage sweep rate.

Conditions	$dE^p/d\log v$ [a]	$dE^p/d\log C_A$ [b]	Theory [c]
AN – HOAc [d,e]	15.1(0.4) ↑	−17.3(0.5) ↓	±18.9
AN [d]	14.1(0.7) ↑	−14.4(1.0) ↓	±16.9

[a] Measurements at 100, 200, 300 and 1000 mV s^{-1} and expressed in mV/decade. The numbers in parentheses are the standard deviations for measurements at concentrations ranging from 0.25 to 1.00 mM. The arrows indicate an increasing trend as C_A was increased. [b] Measurements at C_A ranging from 0.25 to 4.00 mM and expressed in mV/decade. The numbers in parentheses are the standard deviations for measurements at 100 to 1000 mV/s. The arrows indicate a decreasing trend as v was increased. [c] The theoretical value for the EC(dim) mechanism taking into account the temperature. [d] In solvent containing Bu_4NBF_4 (0.1 M) and water (200 – 278 mM). [e] HOAc concentration = 22 mM.

are summarized in Table 9. Either in the presence or absence of HOAc, the slopes are all too low and trends were observed. The trends are designated by the arrows, in the case of $dE^p/d\log v$, an increase in C_A brought about an increase in the slope while an increase in v was in both cases accompanied by a decrease (numerically) in $dE^p/d\log C_A$. The values, especially those for $dE^p/d\log v$ deviate significantly from the theoretical values and the deviations are more serious in the absence of HOAc.

The reaction of MBM with hydroxide ion in acetonitrile. The data in Table 10 indicate that MBM is consumed nearly stoichiometrically upon the addition of Bu_4NOH to a 1.00 mM solution in AN. The reaction apparently occurs as rapidly as mixing takes place and attempts to measure the rate of the reaction by cyclic voltammetry were not successful. The data listed are for peak potential measurements 3 s after mixing was begun and only very small changes could be observed after that time.

DISCUSSION

In formulating a mechanism for the EHD of MBM, the following conclusions based upon the kinetic studies must be taken into account: (i) The reaction, under most conditions is very nearly second order in anion radical and there is no evidence for the involvement of substrate. (ii) Proton donors, either water or acetic acid, have a small or negligible effect on the rate of the reaction. (iii) The apparent activation energy is small and concentration dependent in both AN and DMF. (iv) Base is generated in the EHD and MBM very rapidly reacts with base.

Table 10. The reaction of MBM with hydroxide ion in acetonitrile.

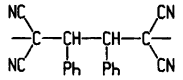
$\lvert Bu_4NOH\rvert$/mM [a]	% MBM Consumed [b]
0.20	25.7
0.40	50.4
0.60	74.2
0.80	95.4

[a] The concentration after addition to a solution of MBM (1.00 mM) in AN containing Bu_4NBF_4 (0.1 M) at 12 °C. [b] Determined by the measurement of the LSV peak current 3 s after mixing was begun.

If we make the assumption that the deviations from the theoretical relationships for the simple dimerization mechanism (1) are primarily caused by the interference of the side reaction between MBM and the base generated during EHD, we can formulate a relatively simple mechanism which takes into account the kinetic observations. Equilibrium (17), which can be viewed as the reversible formation of a dimeric complex of the anion radical, followed by bond forming reaction (18) results in rate law (19). The pre-equilibrium (17) is required

$$2\mathrm{MBM}^{\cdot -} \underset{}{\overset{K_{17}}{\rightleftharpoons}} \mathrm{MBM}^{\cdot -}/\mathrm{MBM}^{\cdot -} \tag{17}$$

$$\mathrm{MBM}^{\cdot -}/\mathrm{MBM}^{\cdot -} \xrightarrow{k_{18}} \tag{18}$$



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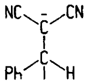
$$\mathrm{Rate} = k_{18}K_{17}\lvert\mathrm{MBM}^{\cdot -}\rvert^2 \tag{19}$$

in order to take into account the concentration dependent, very low activation energy observed in both AN and DMF. The concentration dependence of the activation energy reflects the decreasing importance of equilibrium (17) as the concentration increases in determining the overall activation energy. It is conceivable that at high concentrations equilibrium (17) lies further to the right and the activation energy is almost completely that for reaction (18). This is also supported by the data in Table 8. The greatest changes in E_a are observed at substrate concentrations lower than 1 mM. Between C_A equal 1.0 and 4.0 mM, E_a was observed to increase only slightly from 4.7 to 5.3 kcal/mol.

The kinetic data observed for this system are not unique. It is of interest to compare the structural features of dimeric dianion *4* with those derived from two other anion radicals which dimerize by mechanisms identical to (17)–(18). The two other systems are the anion radicals derived from 9-diazofluorene[16] and anthracenes substituted with electron withdrawing substituents.[17] The observation of activation energies too low for even diffusion controlled reactions required the postulation of equilibria of the type of (17) for both of these systems. A comparison of the partial structures *5*, *6* and *7* reveals that in all three cases, the dimeric dianions have strongly stabilizing structural features, the dicyanomethyl anion (*5*), the acinitro anion (*6*) and the fluorenyl anion (*7*). The kinetics of the three systems are practically identical in most respects. The simplest case involves the dimerization of 9-nitroanthracene anion radical since in this case the product is the stable dianion related to half structure *6*.[17] The apparent activation energy in that case was found to be approximately zero. The rate of dimerization in the latter case was observed to be independent of the water concentration in DMF. These observations led to the conclusion that the mechanism is described by eqn. (20) which is identical to (17)–(18) with the exception that the formation of the dimer dianion was considered to be reversible.



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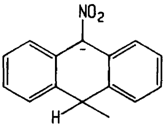

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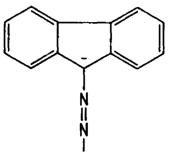


7

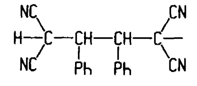
$$2\text{AN}-\text{NO}_2^{\cdot -} \rightleftarrows (\text{AN}-\text{NO}_2^{\cdot -})_2 \rightleftarrows (\text{O}_2\text{N}-\text{AN}-\text{AN}-\text{NO}_2)^{2-} \quad (20)$$

The MBM$^{\cdot -}$ dimerization differs from that of the 9-nitroanthracene anion radical in that the dimeric dianion undergoes further reactions. In view of the product studies by Avaca and Utley[10,11] the most likely reactions following (18) are (21) to (23). These reactions are apparently fast and do not contribute to the rate of the dimerization.

$$4 + \text{ROH} \rightarrow 8 + \text{RO}^- \quad (21)$$

$$8 \rightarrow 9 \quad (22)$$

$$9 + \text{ROH} \rightarrow (2 \rightleftarrows 3) + \text{RO}^- \quad (23)$$



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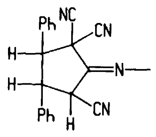


9

We can now examine the conclusions of Nadjo and Savéant[8] in more detail. They concluded that the mechanism does not change when passing from the millimolar to the decimolar concentration range of MBM during the EHD in DMF. They also concluded that residual water plays an important role in the overall reaction and that the formation of an anion radical–water adduct is an essential step as designated by eqn. (4). The dimerization of this anion radical–water adduct (5) was then proposed to play a major role in the formation of hydrodimer. The second conclusion is in sharp contrast to both the kinetic results presented in this paper and to those reported earlier from the same laboratory.[6,7]

First, we can consider the kinetic implications of adduct formation (4) followed by rate determining dimerization (5). The two extreme kinetic cases are when $K_4 \ll 1$ and when $K_4 \gg 1$. The first case gives rise to rate law (24) and the second to (25). In the later case the apparent rate constant would be independent of the water concentration as long as the latter is in excess. On the other hand, rate law (24) predicts a second order dependence on the water concentration. Thus, the case where $K_4 \ll 1$ is immediately ruled out on the basis of the kinetic data. However, we cannot rule out the case where $K_4 \gg 1$ on the basis of kinetics alone since the experimental rate laws are indistinguishable.

$$\text{Rate} = k_{\text{app}} |\text{A}^{\cdot -}|^2 |\text{H}_2\text{O}|^2 \quad (24)$$

$$\text{Rate} = k_{\text{app}} |\text{AS}^{\cdot -}|^2 \quad (25)$$

Table 11. The effect of the water concentration on the peak potential for the reduction of MBM in DMF.[a]

$\|H_2O\|$/mM	R_I'[b]	$-E^p$/mV[c]
<1[d]	0.583(0.002)	1515.0(0.2)
69.5	0.571(0.003)	1510.8(0.2)
139	0.571(0.003)	1512.1(0.4)
278	0.558(0.003)	1514.9(0.2)

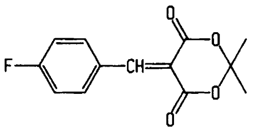
[a] Measurements by derivative cyclic voltammetry at a voltage sweep rate of 97.9 V s^{-1} in solvent containing Bu_4NBF_4 (0.1 M) at 14 °C. $E_{sw}-E_{rev}=300$ mV. [b] The derivative peak ratio. Numbers in parentheses are standard deviations in five measurements. [c] The peak potential *vs.* Ag/Ag^+ measured at a mercury electrode. The numbers in parentheses are standard deviations in five replicates. [d] The solvent electrolyte had been passed through neutral alumina before beginning measurements.

However, the later situation can be evaluated by a consideration of the effect of the water concentration on the reversible potential for the reduction of MBM. The change in reversible potential expected when $K_4 \gg 1$ is given by eqn. (26). When $K_4|H_2O| \gg 1$ the reversible potential is predicted

$$\Delta E^{rev} = (\ln 10)RT/F \log(1 + K_4|H_2O|) \qquad (26)$$

to shift 59.2 mV in the positive direction for each 10-fold increase in the water concentration at 298 K. The data in Table 11 were collected in order to test the effect of water concentration on the reversible potential for the reduction of MBM. The water concentration was varied by more than a factor of 278 with only small variations in the peak potential for the reduction being apparent. The expected result if $K_4|H_2O|$ is large is the E^p should have been shifted by more than 145 mV in the positive direction by the 278-fold increase in $|H_2O|$. Since this was not observed, the involvement of water in the EHD of MBM can be ruled out.

It is not surprising that water is not involved kinetically in the EHD of MBM since we find that HOAc, a very much better proton donor, also only becomes involved after the rate determining steps in the reaction. A similar situation has recently been reported during the EHD of *10* in acetonitrile.[5] This substrate was observed to undergo anion radical – substrate coupling predominantly and the rate of the reaction was not observed to be affected either by HOAc or H_2O. It was proposed that the anion radical is not very basic and this was related to the fact that at pH 5.4, benzylidene Meldrum's acid is half converted to *11*.[18–20]



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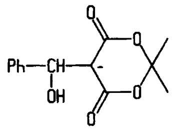
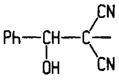


11

We suggested earlier that the small deviations from second order kinetics during the EHD of MBM could be due to the reaction of the substrate with base. The most likely structure of the hydroxide adduct in analogy to *11* is *12*. The rapid consumption of substrate by the base generated during EHD could be responsible for the deviations which Nadjo and Savêant attributed to the involvement of water in the kinetics. In any case, the experimental electrode response when this reaction is taking place could not be expected to be identical to the theoretical response for the simple dimerization mechanism. We clearly see deviations in the LSV and the derivative cyclic voltammetric response. It is somewhat surprising that the convolution potential sweep voltammetry analysis[7] did not show any deviations from the expected response for the simple dimerization in the absence of any complications.



$$Ph-\underset{OH}{CH}-C(CN)_2-$$

12

EXPERIMENTAL

The cells, electrodes, instruments and data handling procedures were the same as used in other papers in this series.[1–5] MBM was prepared by a standard procedure.[21]

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