Mechanisms of the Electrohydrodimerization of Activated Olefins. V.* Substituted Benzylidene Meldrum's Acid Anion Radical Reactions in the Presence of Acetic Acid

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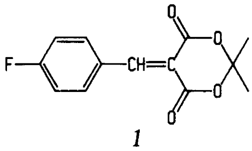
Following the pioneering work of Baizer,[2] electrohydrodimerization of activated olefins has been investigated intensively from both the synthetic and mechanistic viewpoints.[3-5] Primary mechanistic questions are centered around the order of events, *i.e.* whether the initially formed anion radical undergoes dimerization (i), reacts with substrate (ii) or is protonated (iii). Although pathway (i) has been favored by most investigators in this field,[4,5] reaction (ii) has recently been shown to take place when protons are effectively removed from the reaction media.[1b,1c] In the presence of a relatively strong proton donor (phenol) methyl cinnamate was observed to undergo exclusively reaction (iii) but further steps led to the reduced monomer rather than to electrohydrodimerization.[1d] We now report the unexpected results obtained during kinetic studies of the electrodimerization of 4-fluorobenzylidene Meldrums acid (*1*) in acetonitrile in the presence of acetic acid which show that the anion radical does not undergo reaction (iii) even in the presence of the strong proton donor, HOAc. Compound *1* is of special interest in view of the unusual acid-base properties of the parent in the series, which is half converted to *2* at pH 5.4.[6-8]



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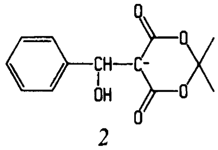

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Derivative linear sweep voltammetry (DLSV)[9] and derivative cyclic voltammetry (DCV)[10-12] kinetic data for the reactions of $1^{\cdot -}$ are summarized in Tables 1–3. The DLSV data can be analyzed using equations (1)–(3).[9] The equations refer to reaction (4) and the lower case letters *a*, *b* and *x* are

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

$$\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_{\mathrm{A}} = [(\ln 10)(a+b-1)/(b+1)]RT/nF \tag{2}$$

$$\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_{\mathrm{x}} = [(\ln 10)x/(b+1)]RT/nF \tag{3}$$

$$\mathrm{A} \pm e^{-} \rightleftarrows \mathrm{B} \xrightarrow{\mathrm{X}} \text{products} \tag{4}$$

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* Parts I–IV, see Ref. 1.

Table 1. The effect of acetic acid concentration on the peak potential sweep rate dependence.[a]

[HOAc]/mM	0.0	4.4	8.8	22.0
$(\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log v)/(\mathrm{mV\ decade}^{-1})$	19.2	19.8	18.9	20.1

[a] In acetonitrile containing Bu_4NBF_4 (0.1 M) and H_2O (278 mM). Peak potentials were measured at a mercury electrode at 18 °C at 100, 200, 400 and 1000 mV s^{-1} with standard deviations of the order of ±0.1 mV. Correlation coefficients were 0.999 or greater at every [HOAc].

Table 2. The effect of the concentrations of the substrate and acetic acid on the linear sweep voltammetry peak potentials.[a]

$v/\mathrm{V\ s}^{-1}$	$(\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_{\mathrm{A}})/(\mathrm{mV\ decade}^{-1})$	$(\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_{\mathrm{X}})/(\mathrm{mV\ decade}^{-1})$
0.200	−31.5(0.987)	−5.6(0.980)
0.400	−28.8(0.997)	−5.6(0.991)
1.000	−26.5(0.999)	−6.3(0.989)

[a] For measurement conditions see Table 1. Measurements were made at $C_{\mathrm{A}} = 0.25$, 0.50, 1.00, 2.00 and 4.00 mM and $C_{\mathrm{X}} = 4.4$, 8.8 and 22 mM. The numbers in parentheses refer to correlation coefficients.

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Table 3. Derivative cyclic voltammetry reaction order study of the hydrodimerization of *p*-fluorobenzylidene Meldrum's acid.[a]

C_A/mM	[H_2O]/mM	[HOAc]/mM	$v_{\frac{1}{2}}$/V s^{-1} [b]	$v_{\frac{1}{2}}/C_A$ [c]	$v_{\frac{1}{2}}/C_A^2$ [d]
0.25	0	0	25.6	102.4	410
0.50	0	0	99.5	199	398
1.00	0	0	309	309	309
0.25	278	22	25.5	102	408
0.50	278	22	66.3	133	265
1.00	278	22	154	154	154

[a] Conditions as in Table 1. [b] The voltage sweep rate necessary for the derivative peak ratio to equal 0.500 as described in Ref. 12. [c] This ratio is constant for second order kinetics.[12] [d] This ratio is constant for third order kinetics.[12]

the reaction orders in A, B and X, respectively, where X is a species in excess which reacts with B. In (1) v refers to the voltage sweep rate. At 18 °C, the theoretical value for $dE^p/d \log v$ is 19.3 mV/decade when b is 2 (eqn. 1). The observed value was found to be independent of [HOAc] under the conditions of the study (Table 1) and equal to 19.5 ± 0.5 mV/decade. On the other hand $dE^p/d \log C_A$ was observed to be dependent upon v (Table 2). Application of (2) with $b=2$ results in values of a, the reaction order in substrate, equal to 0.63 (0.2 V/s), 0.49 (0.4 V/s) and 0.37 (1.0 V/s). The dependence of $dE^p/d \log C_A$ on v is expected when two competing mechanisms with different reaction orders in A are involved.[9] This is because of the concentration gradient of A near the electrode which depends upon v. The apparent reaction order in HOAc, x, was observed to be 0.30 ± 0.02 upon application of eqn. (3) to the data in Table 2.

The DCV reaction order analyses of the reactions of *1* $^{\cdot-}$ in acetonitrile (AN) or AN in the presence of HOAc and H_2O are summarized by the data in Table 3. The apparent reaction order $R_{A/B}$ which may have contributions from both B and A is given by eqn. (5) where $v_{\frac{1}{2}}$ is the value of v necessary for the

$$R_{A/B} = 1 + z\,(v_{\frac{1}{2}}/C_A^z = \text{constant}) \tag{5}$$

derivative peak ratio to equal 0.500. The last two columns in Table 3 show that $v_{\frac{1}{2}}/C_A^z$ is not constant when z is either 1 or 2, the values for $R_{A/B}$ equal to 2 and 3, respectively. The values of z most consistent with eqn. (5) were observed to be 1.75 and 1.3 in the presence and absence of proton donors, respectively. These values correspond to $R_{A/B}$ equal to 2.75 and 2.3.

It is clear from the data discussed to this point that either the mechanism is complex or that competing reactions are involved, both of which are second order in anion radical and one of which gives rise to a rate law including the substrate concentration. Apparent rate constants of complex mechanisms of ion radical reactions very often have low or inverse temperature coefficients.[13] The apparent activation energy for the reactions of electrode-generated intermediates can be obtained directly from eqn. (6) which does not involve

$$\ln v_{\frac{1}{2}}/T = (-E_a/R)(1/T) + c \tag{6}$$

the necessity of the explicit knowledge of rate constants.[14] Analysis of the reactions of *1* $^{\cdot-}$ at 290, 273 and 245 K resulted in $v_{\frac{1}{2}}/T$ equal to 0.46, 0.47 and 0.42, respectively. This gives an apparent E_a of about 0.

All of the data can be accommodated into a reaction scheme involving competing mechanisms (7)–(8) and (9) to generate the dimeric dianion $A^- - A^-$ which then reacts with a proton donor such as acetic acid in (10).

$$A^{\cdot-} + A \rightleftarrows A^- - A^{\cdot} \tag{7}$$

$$A^- - A^{\cdot} + A^{\cdot-} \rightleftarrows A^- - A^- + A \tag{8}$$

$$2\,A^{\cdot-} \rightleftarrows A^- - A^- \tag{9}$$

$$A^- - A^- + \text{HOAc} \rightarrow A^- - A - H + \text{AcO}^- \tag{10}$$

The very low temperature coefficient can be due to reversible reactions (7) and (9). The radical ion – substrate coupling mechanism observed during dimer forming reactions of 4-methoxybiphenyl cation radical has been observed to be accompanied by a near zero apparent activation energy.[15] The fractional orders in substrate and HOAc are accounted for by this scheme as well as is the integral second order in anion radical.

The most significant aspect of the results reported here is that the coupling reactions (7) and (9) occur without the interference of protonation of the anion radicals by acetic acid which only becomes involved after dimer-forming reactions. This must be a consequence of the very weakly basic nature of *1* $^{\cdot-}$

which has structural similarities to *2*. The work also points out that the reversibility of coupling reactions and the feasibility of competitive pathways during electrohydrodimerization contribute to the complexity of the overall mechanism. Further work is in progress in order to clarify the effect of substituents on the rates and mechanisms of the reactions of anion radicals of benzylidene Meldrum's acid.

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