

Mechanisms of the Electrohydrodimerization of Activated Olefins. II. The Radical-Substrate Coupling Mechanism

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Until recently,¹ anion radical coupling was the generally accepted mechanism for electrohydrodimerization (EHD) of activated olefins. In their tenth paper on EHD, Savéant and co-workers² make the general conclusion that the coupling of two anion-radicals is the most probable reaction pathway not only when the observed kinetics are not dependent upon the water concentration but also in the case where they are. One of the model substances, diethyl fumarate, which had previously been investigated intensively,³⁻⁵ has now¹ been shown to give data for EHD in DMF which are incompatible with the anion radical coupling mechanism. In the opinion of the author, the anion radical coupling mechanism for EHD has not been conclusively demonstrated in any case. It was with this purpose in mind that the present investigation was undertaken. Methyl cinnamate was chosen as a model substance since one of the most recent EHD studies claimed to demonstrate the anion radical coupling mechanism in this case.⁶

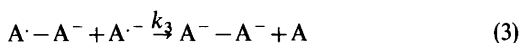
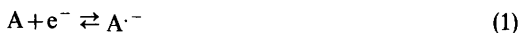
Since the kinetic involvement of H₂O has been demonstrated during EHD of diethyl fumarate in DMF,¹ it is necessary to work in as water-free solution as possible in order to attempt to demonstrate the anion radical coupling mechanism. Anhydrous conditions can be realized by carrying out voltammetry on solutions over neutral alumina.⁷ Acetonitrile was chosen as solvent since the EHD kinetics for methyl cinnamate have been reported to be nearly independent of the water concentrations in the latter while the rate in DMF is increased by the addition of water.²

Derivative cyclic voltammetry⁸ kinetic data for the EHD of methyl cinnamate are summarized in Table 1. In the table $v_{\frac{1}{2}}$ is the voltage sweep rate at which the derivative peak ratio is equal to 0.500 as recently described.⁹ For a reaction second order in anion radical $v_{\frac{1}{2}}/C_A$, where C_A is the substrate concentration, should be constant. The first three rows in the table indicate that with [H₂O] in acetonitrile equal to 136 mM, second order behaviour is indeed observed with $v_{\frac{1}{2}}/C_A$ equal to 4.11 ± 0.18 . However, in "anhydrous" acetonitrile the reaction is clearly of higher order. The value of

$v_{\frac{1}{2}}/C_A$ increases by nearly a factor of three in going from C_A equal to 1.0 mM to 8.0 mM. In fact a two-fold increase in C_A very nearly results in a three-fold increase in $v_{\frac{1}{2}}$. Another significant feature of the data is that the rate of the reaction is enhanced by an order of magnitude in the presence of water (136 mM). Two conclusions are unavoidable from these data. First, the mechanism differs in the presence and the absence of water and second, water is kinetically involved in the one case.

The observed second order rate constant for the reaction in the presence of water was found to be $2.71 (0.12) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. It is of interest to note that this is more than a factor of 10^2 greater than that observed for diethyl fumarate anion radical in DMF with approximately the same water concentration.¹ In order to determine whether this is due to a solvent effect or to structural differences, kinetic experiments were carried out on diethyl fumarate under the same conditions as for the data in Table 1. The rate constant was found to be slightly greater than that for methyl cinnamate under comparable conditions.

The most significant aspect of the data is that a higher order mechanism is involved when water is excluded. The most likely mechanism is the radical-substrate coupling reaction (2) followed by rate determining electron transfer (3). This mechanism



$$\text{rate} = k_2 k_3 [A^{\cdot -}]^2 [A] \quad (4)$$

Table 1. Kinetics of the electrohydrodimerization of methyl cinnamate in acetonitrile.^a

[MC]/mM	[H ₂ O]/mM	$v_{\frac{1}{2}}/V \text{ s}^{-1}$	$v_{\frac{1}{2}}/C_A/V \text{ s}^{-1} \text{ mM}^{-1}$
1.00	136	4.20	4.20
2.00	136	7.80	3.90
4.00	136	16.90	4.23
1.00	<1	0.350	0.350
2.00	<1	0.970	0.485
4.00	<1	2.52	0.625
8.00	<1	6.95	0.869

^a Measured by derivative cyclic voltammetry in solvent containing Me₄NBF₄ (0.05 M) at 18.5 °C. $v_{\frac{1}{2}}$ refers to the voltage sweep rate at which the derivative peak ratio is equal to 0.500.

gives rise to rate law (4) assuming the steady state approximation for $A^{\cdot-} - A^-$ and that $k_2[A] \gg k_3[HA^{\cdot-}]$. In order to get an idea of the magnitudes of the rate constants and concentrations necessary for (4) to describe the reaction, we can estimate k_3 to be $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Then, if k_2 is equal to $10^6 \text{ M}^{-1} \text{ s}^{-1}$, it is necessary for $[A]/[A^{\cdot-} - A^-]$ in the reaction layer to be of the order of 10^4 in order for (2) and (3) to proceed at the same rate. In order to subject rate law (4) to a further test, linear sweep voltammetry studies were carried out on the diethyl fumarate system in "anhydrous" acetonitrile containing Me_4NBF_4 . Rate law (4) predicts a value of 39.4 mV/decade at 298 K for the substrate concentration dependence.¹⁰ The observed value at 22 °C was 36.8 ± 2.3 mV for four determinations. Thus, all of the data in "anhydrous" acetonitrile are consistent with the radical-substrate coupling mechanism. The failure to observe this mechanism earlier must be a consequence of the fact that solvent-electrolyte systems always have appreciable water content unless extreme precautions^{7,11} are taken to keep the systems anhydrous. Since it is now recognised¹ that water does intervene in EHD reactions which have previously been believed to be of the anion radical coupling type, all previous work on EHD reactions which has been conducted on systems containing at least trace amounts of water is questionable. The two cases tested, methyl cinnamate and diethyl fumarate, do not involve the anion radical coupling mechanism. Whether or not this mechanism takes place in any EHD reactions remains to be established.

In conclusion, it should be noted that the radical-substrate coupling mechanism has been demonstrated in a related case, the dimer forming reaction of 4,4'-dimethoxystilbene cation radical¹² which had previously been believed to follow the cation radical dimerization mechanism.^{13,14}

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