

The Anion Radical-Proton Donor Complex Mechanism of the Electrohydrodimerization of Diethyl Fumarate in *N,N*-Dimethylformamide

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Electrohydrodimerization of activated olefins has been the subject of numerous investigations.¹⁻¹⁴ Although other mechanisms have been suggested,¹ there now seems to be general agreement that the reactions follow a mechanism in which the key step is the dimerization of the anion radicals. Diethyl fumarate (DEF) has been intensively investigated as a model substrate for the electrohydrodimerization (EHD) reaction.^{3,8,10} The rate constant for the dimerization of DEF^{•-} in *N,N*-dimethylformamide (DMF) at 25 °C was suggested to be equal to 37 M⁻¹ s⁻¹ and the activation energy was found to be 4.2 kcal mol⁻¹.³ The very low second order rate constant and an activation energy of the order expected for very rapid reactions approaching the diffusion controlled limit appeared to be inconsistent and warranted further investigation.

The reason for the inconsistency noted above is suggested by the fact that the rate of the EHD reaction was found to be dependent upon the concentration of water present.³ However, double potential step chronoamperometry (DPSC) data either under anhydrous conditions or in the presence of water up to 150 mM fit the anion radical dimerization working curve and were inconsistent with theoretical data for other mechanistic schemes simulated. On this basis, it was proposed that the role of water was to specifically solvate the anion radicals and hence increase the dimerization rate.

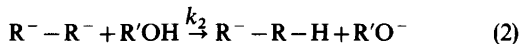
In order to test for the kinetic involvement of water in the EHD reaction of DEF, measurements were made on solutions of DEF in DMF containing H₂O and D₂O at various concentrations. The first three rows of data in Table 1 confirm that the reaction is second order in DEF in the presence of water and the observed rate constant compares favorably with that previously reported when the water concentration is taken into account. The next four rows of data show that the reaction is very nearly first order in [H₂O] under the conditions of the experiments. The final four rows contain data obtained when D₂O was the proton donor. Once again, the reaction is very nearly first order in the proton donor.

Table 1. Kinetics of the electrohydrodimerization of diethyl fumarate in *N,N*-dimethylformamide.^a

| [DEF]/mM | [H ₂ O]/mM | $v_{\frac{1}{2}}^b/V$ s ⁻¹ | k^c/M^{-1} s ⁻¹ |
|----------|-----------------------|---------------------------------------|------------------------------|
| 3.07 | 278 | 0.145 | 311 |
| 6.14 | 278 | 0.34 | 364 |
| 12.3 | 278 | 0.65 | 348 |
| 11.5 | 139 | 0.30 | 172 |
| 11.5 | 278 | 0.60 | 343 |
| 11.5 | 417 | 0.865 | 495 |
| 11.5 | 556 | 1.12 | 641 |
| 11.5 | 139 ^d | 0.28 | 160 |
| 11.5 | 278 ^d | 0.53 | 303 |
| 11.5 | 417 ^d | 0.775 | 443 |
| 11.5 | 556 ^d | 1.00 | 572 |

^a Measured at a gold electrode in solvent containing Bu₄NBF₄ (0.1 M) at 22 °C by derivative cyclic voltammetry according to Ref. 16. ^b The voltage sweep rate necessary for the derivative peak ratio, R'_p , to equal 0.500 according to Ref. 17. ^c Calculated according to Ref. 17. ^d Concentration of D₂O in mM.

If one attempts to include a protonation step in the anion radical dimerization scheme (eqns. 1 and 2), analysis results in rate law (3). The two limiting



$$\text{Rate} = k_1[R^{\bullet-}]^2[R'OH]/(k_{-1}/k_2 + [R'OH]) \quad (3)$$

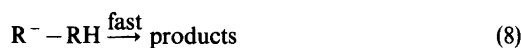
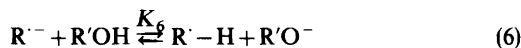
cases of (3), depending on the relative magnitudes of the terms in the denominator are (4) and (5). Either of these rate laws fit the EC(dim) scheme as

$$\text{Rate} = k_2K_1[R^{\bullet-}]^2[R'OH] \quad (4)$$

$$\text{Rate} = k_1[R^{\bullet-}]^2 \quad (5)$$

long as the proton donor (ROH) is in excess, but only (4) takes into account the kinetic involvement of the proton donor and predicts a primary kinetic isotope effect. In order to arrive at (4) it was necessary to assume that $k_{-1}/k_2 \gg [ROH]$. This assumption does not appear to be justifiable. Reverse reaction (1) involves the cleavage of a C-C bond which is not expected to be facile even though it may be accelerated in this case by charge repulsion. Reaction (2) on the other hand should be very rapid since it involves proton transfer from oxygen and K_2 can be estimated to be of the order of 10⁹ from the relative pK_a values of H₂O and ROOCCH₂R. Thus, the data appear to be inconsistent with the anion radical coupling mechanism.

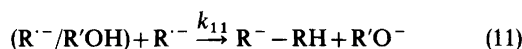
The observed deuterium isotope effect, 1.11 ± 0.03 , is indicative that the proton transfer occurs in an equilibrium since K_H/K_D is normally close to unity while k_H/k_D is generally >2 for primary kinetic isotope effects.¹⁵ Equilibrium (6) followed by (7) and (8) gives (9) which is consistent with the



$$\text{Rate} = k_{\text{obs}}[R^{\cdot-}]^2[R'OH]/[R'O^-] \quad (9)$$

reaction orders in anion radical and proton donor but requires a -1 order in $[R'O^-]$ which is not observed.

A mechanism which is consistent with all of the kinetic data involves equilibrium (10) followed by (11) and finally (8), resulting in rate law (12). Equi-



$$\text{Rate} = k_{\text{obs}}(R^{\cdot-})^2[R'OH] \quad (12)$$

librium (10) can be regarded as the reversible formation of a complex between $R^{\cdot-}$ and $R'OH$ in which transfer of the proton does not occur, at least not to the extent that RO^- becomes kinetically involved. It should be observed that the anion radical serving as reductant in (11) is not complexed with the proton donor. This is further evidence that the anion radical/proton donor complex is a distinct species and that the rate enhancement by water is not due to a general solvation effect. The low activation energy is readily accounted for by the complex reaction scheme providing that K_{10} is inversely affected by the temperature.

Extrapolation of the data in Table I to zero water content indicates a "residual" rate constant of the order of $25 \text{ M}^{-1} \text{ s}^{-1}$. The proton donor for this reaction could be the water introduced by the solvent-electrolyte system or possibly even the supporting electrolyte. Thus, there is no evidence for the coupling of two anion radicals as previously proposed.^{3,8,10}

REFERENCES

1. Petrovich, J. P., Baizer, M. M. and Ort, M. R. *J. Electrochem. Soc.* 116 (1969) 743, 749.
2. Andrieux, C. P., Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem.* 26 (1970) 147; 42 (1973) 223.
3. Childs, W. V., Maloy, J. T., Keszthelyi, C. P. and Bard, A. J. *J. Electrochem. Soc.* 118 (1971) 874.
4. Puglisi, V. J. and Bard, A. J. *J. Electrochem. Soc.* 119 (1972) 829, 833; 120 (1973) 748.
5. Bard, A. J., Puglisi, J. V., Kenkel, J. V. and Lomax, A. J. *Chem. Soc. Faraday Discuss.* 56 (1973) 353.
6. Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem.* 44 (1973) 748.
7. Lamy, E., Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem.* 42 (1973) 189; 50 (1974) 141.
8. Grypa, R. D. and Maloy, J. T. *J. Electrochem. Soc.* 122 (1975) 377, 509.
9. Vartires, I., Smith, W. H. and Bard, A. J. *J. Electrochem. Soc.* 122 (1975) 894.
10. Hazelrig, M. T. and Bard, A. J. *J. Electrochem. Soc.* 122 (1975) 211.
11. Klemm, L. H. and Olsen, D. R. *J. Org. Chem.* 38 (1973) 3390.
12. Bezilla, B. M., Jr. and Maloy, J. T. *J. Electrochem. Soc.* 126 (1979) 579.
13. Nadjo, L., Savéant, J. M. and Tessier, D. *J. Electroanal. Chem.* 64 (1975) 143.
14. Yeh, L. R. and Bard, A. J. *J. Electrochem. Soc.* 124 (1977) 189, 355.
15. More O'Ferrall, R. A. In Caldin, E. F. and Gold, V., Eds., *Proton-Transfer Reactions*, Chapman and Hall, London 1975, Chapter 8.
16. Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem. In press.*
17. Parker, V. D. *Acta Chem. Scand. B* 35 (1981). *In press.*

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