

SHORT COMMUNICATION

Electrodimerization

X. Solvation and protonation in the EHD of activated olefins in low acidity media

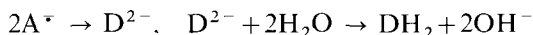
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(Received 14th June 1973)

In the fifth paper of this series¹, the mechanism of the electrohydrodimerization (EHD) of activated olefins was investigated in low acidity media, namely acetonitrile (ACN), dimethylformamide (DMF) and, in a few cases, ethanol buffered with tetrabutylammonium hydroxide. The analysis of the mechanism was mainly based on the observed rates of variation of the peak potential (E_p) in linear sweep voltammetry (LSV) with the sweep rate (v), the initial concentration (c^0) and the amount (Z^0) of a proton donor, water in most cases, present in the solution. Two situations depending on the particular compound considered and on the proton donor concentration range were discussed successively:

(i) In the first case, the observed kinetics are independent of the amount of water present, *i.e.*, E_p does not vary significantly with this factor. Under these conditions, the analysis of the kinetic results shows without ambiguity that the mechanism of the EHD involves a rate-determining radical coupling of two anion-radicals followed by rapid protonation of the dimer di-anion formed:



without detectable interference of radical-substrate or ion-substrate coupling steps.

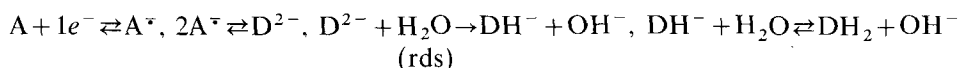
(ii) In the second case, the observed kinetics depend on the quantity of water added to the solution. E_p varies with this quantity, in general slightly for the first additions and more markedly for further ones. Protonation reactions, involving in particular the conversion of the anion-radical A^\cdot into the neutral radical AH^\cdot were considered as the only possible cause of these variations. This is in fact not quite correct since solvation of the anion-radical without appreciable conversion into AH^\cdot may also be responsible for the observed dependence upon the amount of water in solution.

It is the purpose of the present communication to discuss the respective roles of protonation and solvation on the basis of previous experimental data¹ and of some additional results. Let us consider successively these two possibilities and their implications on the determination of the mechanism.

Protonation

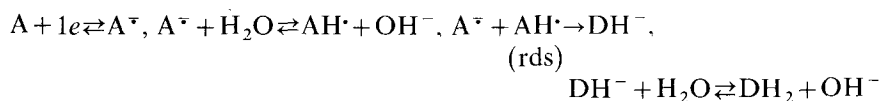
A detailed analysis of the formal kinetics of EHD involving the role played by the protonation reactions is now available² (see particularly Tables 2 and 4 in ref. 2 on which the present discussion is based).

Consider first the radical-radical coupling type reaction schemes. According to the experimental values of $\partial E_p / \partial \log v$, $\partial E_p / \partial \log c^0$ and $\partial E_p / \partial \log Z^0$, the first possibility is the e-rrc-P-p reaction scheme:



If such a reaction sequence were occurring the progressive addition of water would first lead to a 19.7 mV variation and then to a steady value of E_p when the coupling step has become rate determining due to the acceleration of the protonation step. The observed behaviour is just the opposite.

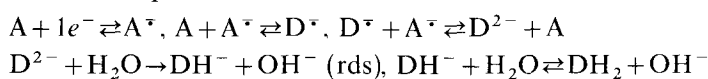
The experimental values are also *a priori* compatible with the e-p-RRC-p scheme:



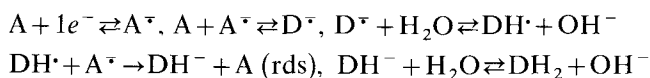
in a buffered medium but not in an unbuffered one. The media actually used were not buffered except in one case. It follows that this mechanism must also be rejected unless the medium is assumed to be accidentally buffered¹ because of a rapid attack of OH^- on the solvent or the supporting electrolyte cation leading to a stationary OH^- concentration. Actually, this does not seem very likely since these reactions are not likely to be that fast.

Concerning the radical-substrate coupling mechanisms, the following three possibilities must be discussed according to the observed rates of the E_p variations:

-e-rsc-d-P-p:

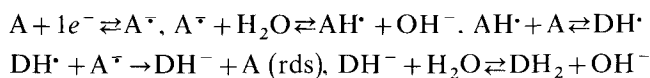


-e-rsc-p-D-p in unbuffered medium:



These two mechanisms must also be rejected since they imply that the way in which A^\cdot leads to a dimeric species would change with the amount of water added from a radical-radical type reaction to a radical-substrate type one.

-e-p-rsc-D-p:



This reaction scheme is perfectly compatible with the kinetic results. It involves a radical attack of the neutral radical on the double bond of the starting material. However, such a radical attack on the double bond is likely to

proceed beyond the dimer leading to polymer formation. So, addition of a proton donor would result in an increased quantity of polymer. As shown by our own results¹ and many others^{3,4} the observed trend is the opposite. This radical-substrate type mechanism is thus unlikely for chemical reasons.

Ion-substrate couplings are not compatible with the LSV data. They have also been rejected on the basis of the observed variations of the polarograms upon addition of water.

It follows that protonation of the anion-radical does not seem to be responsible for the observed shifts of E_p with addition of water.

Solvation

Among the various anionic species A^\cdot , A^{2-} , D^\cdot , D^{2-} that may be formed during the electrodimersation process, only A^\cdot may not be protonated by water. The others are very likely to be protonated since the mesomery of the doublet and the odd electron in A^\cdot is not possible in A^{2-} and D^{2-} as well as in D^\cdot .

If, thus, A^\cdot is assumed to be solvated and not protonated by the added water, the only possible reaction sequence is $e-RRC-p-p: A + 1e^- \rightleftharpoons A^\cdot, 2A^\cdot$ (solvated by H_2O) $\rightarrow D^{2-}$ (rds) $D^{2-} + 2H_2O \rightarrow DH_2 + OH^-$ as in the case where E_p is independent of the water addition.

Now, the variation of E_p with the amount of water present can be attributed to the fact that the coupling of two anion radicals is easier when they are surrounded by more water molecules.

That the anion radicals are actually solvated by the water present in the medium is clearly seen in Table 1, where the column $\partial E_1^0 / \partial \log Z^0$ shows the variations of the horizontal part of the $E_p - \log v$ plots (Fig. 1) with the quantity of water present. This shift may not exactly represent the variations of the standard potential E_1^0 of the couple A/A^\cdot since part of it may result from a variation in the reference electrode potential. However, this is probably a small

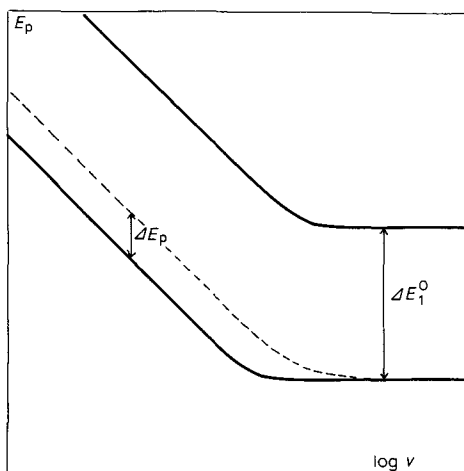
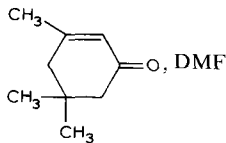


Fig. 1. Measurement of $(\partial E_1^0 / \partial \log Z^0)$ and $(\partial E_p / \partial \log v)$.

TABLE 1
 PEAK POTENTIAL AND A/A^* STANDARD POTENTIAL vs. WATER CONCENTRATION

H_2O vol. %	$(\partial E_p / \partial \log Z^0) / mV$	$(\partial E_1^0 / \partial \log Z^0) / mV$
α -Cyanoethylcinnamate $C_6H_5-CH=C(CN)CO_2C_2H_5$, ACN		
0.05	negl.	18
5		
Methylcinnamate $C_6H_5-CH=CH-CO_2CH_3$, ACN		
0.05		
1	6	9
2	20	50
Methylcinnamate $C_6H_5-CH=CH-CO_2CH_3$, DMF		
5		
20	20	33
Ethylcinnamate $C_6H_5-CH=CH-CO_2C_2H_5$, ACN		
0.05		
1	5	19
Ethylcinnamate $C_6H_5-CH=CH-CO_2C_2H_5$, DMF		
5		
10	16	53
Chalcone $C_6H_5-CH=CH-CO-C_6H_5$, ACN		
0.05		
1	6	38
5	23	100
Chalcone $C_6H_5-CH=CH-CO-C_6H_5$, DMF		
0.1		
1	4	16
	6	75
10	17	130
20		
Benzalacetone $C_6H_5-CH=CH-CO-CH_3$, ACN		
0.05		
0.5	17	30
5	17	120
Benzalacetone $C_6H_5-CH=CH-CO-CH_3$, DMF		
0.1	negl.	25
1	negl.	70
5	negl.	133
10		
Mesityl oxide $(CH_3)_2C=CH-CO-CH_3$, DMF		
0.1		
1	negl.	65
Isophorone		
		
0.1		
1	negl.	70

amount of the total shift. The column $\partial E_p / \partial \log Z^0$ represents the effect of the addition of water on the rate of the coupling process itself since it results from measurements performed in the way shown in Fig. 1.

It is seen that a positive shift of E_1^0 corresponds either to a negligible variation or to an increase of the coupling rate in accordance with the fact that an increased solvation of the anion-radical by water facilitates the coupling to an extent that depends on the particular compound considered.

It is to be noted that even the experiment¹ performed with benzalacetone in ethanol buffered with Bu_4NOH is not actually inconsistent with the e-RRC-p-p reaction scheme. Indeed, the observed increase in the coupling rate, on passing from ACN and DMF to this medium (see Table 6 in ref. 1), may be attributed to increased solvation and not necessarily to the protonation of the anion-radical.

Our general conclusion is thus that the *coupling of two anion-radicals* is the most probable reaction path in the EHD of activated olefins not only when the observed kinetics are not dependent upon water addition but also in the case where they are. Let us emphasize again that this conclusion concerns low acidity media and substrate concentrations in the millimolar range.

REFERENCES

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- 4 M. M. Baizer and J. P. Petrovich in A. Streitwieser and R. W. Taft (Eds.), *Progress in Physical Organic Chemistry*, Vol. 7, Interscience, New York, 1970, pp. 189-227.