

Mechanisms of the Electrodimerization of Activated Olefins. VIII. Negative Activation Enthalpies in the Dimerization of Diethyl Fumarate Anion Radical

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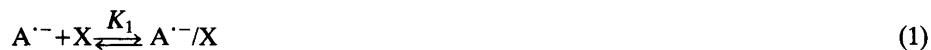
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Electrode kinetic studies were carried out on the electrohydrodimerization of diethyl fumarate in acetonitrile containing water. The reaction was observed to be second order in anion radical and approximately first order in water. Over a wide range of water concentration the enthalpy of activation was observed to be of the order of -4 kcal/mol with an entropy of activation close to -50 cal/K mol. The mechanism of the reaction consists of hydrogen bonding equilibrium (i) followed by rate determining coupling reaction (ii).



The mechanism is discussed in relation to other cases in reactive intermediate chemistry where negative activation enthalpies are observed.

The previous paper⁷ in this series¹⁻⁷ dealt with the examination of rate-activation energy relationships for the dimerization reactions of ion radicals. Experimental results were presented for the dimerization of diethyl fumarate (DEF) anion radical in *N,N*-dimethylformamide (DMF) containing water and sometimes alkali metal cations. The reactions were found to follow general mechanism (1)-(2) in which X was either



water, hydrogen bonded to the solvent, or alkali metal cation and $\text{A}^{\cdot-}$ is the anion radical of the substrate. Simple dimerization of the anion radical (3) was not observed and it was proposed that



about $10 \text{ M}^{-1}\text{s}^{-1}$ is the maximum value of k_3 at ambient temperature. When X was water, ΔH^\ddagger was observed to be 1.3 kcal/mol. It was also possible to determine ΔH_1^\ddagger for reaction (1) to be equal to -5.9 kcal/mol. Thus ΔH_2^\ddagger is of the order of 7.2 kcal/mol and ΔH_3^\ddagger was estimated to be of the order of 11 kcal/mol or greater. The general conclusion of the study was that the activation parameters of ion radical reactions are not unusual in comparison to those for other reactive intermediate reactions and are a valuable guide in assigning mechanisms for complex reactions. The use of such arguments had previously been questioned and it had incorrectly been suggested that the procedure neglects results from classical chemical kinetics.⁸

The very low ΔH^\ddagger observed for the dimerization of $\text{DEF}^{\cdot-}$ in DMF, *i.e.* 1.3 kcal/mol, is clearly out of the range expected for a reaction with a second order rate constant at room temperature of the order of $400 \text{ M}^{-1}\text{s}^{-1}$ (at a water concentration of 0.5 M). Diffusion controlled reactions are expected to have activation energies of the order of 3 kcal/mol in this solvent.⁹ However, as long as ΔH^\ddagger is positive, even though very small, arguments for a simple mechanism can be made using non-specific steric factors or ineffective collisions as the basis for unusual rate-activation parameter relationships. Such arguments have recently been invoked in related studies.^{8,10}

In this paper we report the results of a kinetic investigation of the dimerization of $\text{DEF}^{\cdot-}$ in acetonitrile. This study resulted in the first observation of negative enthalpies of activation for electrohydrodimerization of activated olefins. The results strongly support the earlier discussion⁷ concerning rate-activation parameter relationship. The only previous reports of negative activation enthalpies for electro-dimerization that we are aware of were from this laboratory and deal with dimerization of 9-substituted anthracene anion radicals¹¹ and the formation of dithionate from sulfur dioxide anion radical.¹²

RESULTS

Kinetic Method. The kinetics of the reactions of $\text{DEF}^{\cdot-}$ were investigated using double potential step chronoamperometry (DPSC).¹³ The cyclic voltammetric peaks for the formations and oxidation of the anion radical were first centered in a 600 mV sweep interval, the extremes of which were then used for the potential step experiments. Rate constants were then calculated from theoretical data for a second order reaction of the anion radical.

Table 1. Reaction order data for the dimerization of diethylfumarate anion radical in acetonitrile.^a

$[\text{H}_2\text{O}]^b/\text{mM}$	$[\text{DEF}]^b/\text{mM}$	T/K	$R_{\text{A/B}}^c$	B_x^d
69	v	291	1.9	
139	v	291	1.9	
v	0.50	273		1.2
v	1.0	273		1.2
v	2.0	273		1.1
v	4.0	273		1.2
v	8.0	273		1.3

^a Kinetic measurements by double potential step chronoamperometry in solvent containing Bu_4NBF_4 (0.1 M). ^b Entries labelled v indicate that this was the variable in the set of experiments. ^c The sum of the reaction orders in $\text{DEF}^{\cdot-}$ over $[\text{DEF}]$ ranging from 0.50 to 4.0 mM. ^d The reaction order in water over the concentration range, 69 to 555 mM.

Table 2. Kinetic and activation parameters for the dimerization of diethylfumarate anion radical in acetonitrile.^a

[H ₂ O]/mM	[DEF]/mM	ΔH^\ddagger /(kcal/mol)	ΔS^\ddagger /(cal/K mol)	$10^{-3}k^b/M^{-1}s^{-1}$
35	4.0	-4.1	-56	5.5
35	8.0	-3.3	-53	7.8
69	2.0	-3.9	-53	17.3
69	4.0	-3.0	-50	16.1
69	8.0	-3.3	-51	18.5
139	1.0	-3.7	-51	34.7
139	2.0	-3.8	-52	33.5
139	4.0	-3.0	-48	38.0
278	0.25	-3.5	-4.8	107
278	0.50	-4.4	-52	94
278	1.0	-3.6	-49	91
278	2.0	-4.0	-51	81
417	0.25	-3.7	-48	165
417	0.50	-4.3	-50	219
417	1.0	-3.5	-47	146
555	0.25	-3.9	-48	279
555	0.50	-4.3	-49	266
555	1.0	-3.2	-46	222
		-3.7 ± 0.4	-50 ± 2	

^a In solvent containing Bu₄NBF₄ (0.1 M) at temperatures ranging from 273 to 293 K. ^b The pseudo second order rate constant at 273.2 K.

Kinetic Results. Reaction orders in water and in anion radical were determined using as wide as possible variation of water and DEF concentrations, respectively, in the usual manner.¹⁴ The data are summarized in Table 1. The reaction order in DEF^{•-} was observed to be 1.9 and that in water 1.2 indicating a reasonably good fit to rate law (4), which is

$$-d[\text{DEF}^{\bullet-}]/dt = k_2 K_1 [\text{DEF}^{\bullet-}]^2 [\text{H}_2\text{O}] \quad (4)$$

consistent with mechanism (1)+(2). The slightly greater than unity reaction order in water could be due to a small contribution from reaction (5).



However, this does not explain the small discrepancy in the anion radical reaction order. In any event the reaction order data support mechanism (1)+(2) as the predominant reaction pathway.

Two detailed sets of experiments were carried out to determine the activation parameters of the dimerization reaction. Data are reported in Table 2 for the solvent/electrolyte, acetonitrile/Bu₄NBF₄ (0.1 M) and in Table 3 for acetonitrile/Bu₄NBF₄ (0.05 M). The water concentration was varied from 0.035 to 0.555 M and substrate concentrations from 0.25 to 8 mM were used. At the higher supporting electrolyte concentration (0.1 M), ΔH^\ddagger was observed to be -3.7 ± 0.4 kcal/mol while ΔS^\ddagger was -50 cal/K mol. Essentially identical results were obtained at the lower electrolyte concentration (Table 3). In this case values of -3.5 ± 0.4 kcal/mol and -50 cal/K mol were observed for ΔH^\ddagger and ΔS^\ddagger ,

Table 3. Kinetic and activation parameters for the dimerization of diethylfumarate anion radical in acetonitrile.^a

[H ₂ O]/mM	[DEF]/mM	ΔH^\ddagger /(kcal/mol)	ΔS^\ddagger /(cal/K mol)	$10^{-3}k^b/\text{M}^{-1}\text{S}^{-1}$
69.4	2.0	-3.3	-51	16.2
139	1.0	-3.2	-48	32.3
139	2.0	-3.1	-48	46.3
278	0.5	-3.8	-50	81.6
278	1.0	-4.3	-51	83.6
		-3.5 ± 0.4	-50 ± 1.1	

^a In solvent containing Bu₄NBF₄ (0.05 M), at temperatures ranging from 273 to 293 K. ^b The pseudo second order rate constant at 273.2 K.

respectively. The variations in the value of $k_{273.2}$, the pseudo-second-order rate constant at constant [H₂O] at different substrate concentrations suggest that the observed deviations in reaction orders mentioned earlier may well be due to error introduced by the fact that the electrode response is not ideal. It is commonly observed that processes affected by adsorption become less ideal as the amount of water in non-aqueous solvents is increased. The standard deviations in the activation parameters, considering the wide range of experimental conditions lends a considerable degree of confidence to the mean values.

Attempts to Determine Equilibrium Constants for Reaction (1). A number of attempts were made to determine the equilibrium constants for the formation of DEF^{•-}/H₂O using phase selective second harmonic *a.c.* voltammetry. The equilibrium constants observed depended strongly on the measurement parameters, differing with frequency and phase. The observed values also were dependent upon the substrate concentrations which suggests interference from the kinetics. It was concluded that reliable results could not be obtained and attempts were discontinued.

DISCUSSION

Practically all simple one-step chemical reactions exhibit appreciable positive activation enthalpies. For second order reactions involving neutral reactants and products, the charge contribution to ΔH^\ddagger is expected to be minimal and in many cases orbital factors predominate. Even second order reactions between ions of opposite charge are not always diffusion controlled reflecting the fact that orbital considerations can be a factor even in these cases. The dimerization of ion radicals represents a special case. Since the reactants in these reactions are of the same charge, the charge contribution inhibits the reaction and both charge and orbital factors contribute to making ΔH^\ddagger more positive. We are not aware of authentic simple second order reactions with activation enthalpies less than those for the corresponding diffusion controlled reactions in the particular solvent system. Thus, it would appear that comparing ΔH^\ddagger with second order rate constants for a reaction should provide a useful criterion to use in deciding whether a reaction is of the simple one step variety or more complex. For example, if ΔH^\ddagger for a reaction in DMF is observed to be less than about 2 kcal/mol, the value for diffusion in that solvent,⁹ and the rate constant at ambient temperature is considerably less than about $10^9 \text{ M}^{-1}\text{s}^{-1}$, it is highly likely that the reaction is more complex than a simple one step reaction. This is not in any way meant to imply that activation entropies cannot be greater than those for diffusion. The argument is based upon

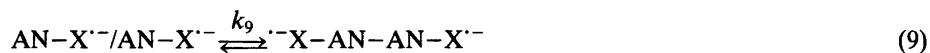
the activation energy-rate constant relationship expected to prevail under most circumstances.

So far we have been unable to establish the existence of any simple one step rate determining dimerizations of anion or cation radicals. The dimerization of 9-substituted anthracene anion radicals was expected to fall in this category since the products are stable dianions and under conditions where the dissociation of the dianions can be neglected the kinetics indicate rate law (6).¹⁵ However, the activation parameters are not consistent with simple reaction (7).¹¹ Activation enthalpies of 1.2 and -0.2 kcal/mol were observed in DMF for anion radicals where X is CN and NO₂, respectively.

$$\text{Rate} = k_{\text{app}}[\text{AN-X}^{\cdot-}]^2 \quad (6)$$



The corresponding values of k_{app} at 20 °C were of the order of 2×10^5 and 2×10^6 M⁻¹s⁻¹, respectively. A more recent study on the dimerization of AN-CN^{·-} in various solvents has substantiated the earlier studies and in one case a negative ΔH^\ddagger was found for this reaction as well.¹⁶ Thus, the mechanism of this reaction must accommodate this. A mechanism consistent with the data involves the initial association into a complex (8) followed by rate determining bond formation (9).^{11,15}



The pre-equilibrium association of DEF^{·-} with water (1) followed by rate determining coupling reaction (2) is a somewhat more clearly defined mechanism.^{1,7} While there is no information on the nature of the dimeric dianion complex in reaction (8), equilibrium (1) is quite well defined. It is known that water is strongly hydrogen bonded to DMF and other aprotic solvents and a number of examples of hydrogen bonding equilibria (1) have been investigated.¹⁷⁻¹⁹ The pertinent activation and thermodynamic parameters have been evaluated in DMF. The apparent activation enthalpy was observed to be comprised of a negative ΔH_1° (-5.9 kcal/mol) and a positive ΔH_2^\ddagger (7.2 kcal/mol) with an overall value less than expected for a diffusion controlled reaction while the rate constant at ambient temperature was about 7 orders of magnitude less than expected if the reaction were controlled by diffusion of the reactants.

The dimerization of DEF^{·-} in acetonitrile (Tables 1-3) fits the general criteria expected for mechanism (1)+(2). In this case we have been unable to study equilibrium (1) and thus our apparent activation enthalpies cannot be broken down into the constituent thermodynamic and activation contributions. However, the fact that $\Delta H_{\text{app}}^\ddagger$ is strongly negative in this case (-3.7 kcal/mol) there is little doubt about the complex nature of the reaction. The reaction order data are in reasonable accord with pre-equilibrium mechanism (1)+(2). Aside from the small inconsistencies noted earlier, it appears safe to conclude that there is no mechanism change in going from DMF to acetonitrile as solvent. The negative $\Delta H_{\text{app}}^\ddagger$ suggests a more dominating role of ΔH_1° in this case.

The observations of low and negative activation enthalpies have recently become a rather common phenomenon. The explanation for the energetics of these reactions is that

the reactions proceed through at least one intermediate, present in low concentration and usually referred to as a complex. This general reaction scheme is illustrated by eqns. (10)+(11) and gives rise to rate law (12). Because the heat of formation of the complex, ΔH_{10}° , can be negative, the overall activation enthalpy, $\Delta H_{app}^{\ddagger}$, which is made up of two terms (13) may assume appreciable negative values.



$$\text{Rate} = (k_{10}k_{11}/(k_{-10}+k_{11}))[A][B] \quad (12)$$

$$\Delta H_{app}^{\ddagger} = \Delta H_{10}^{\circ} + \Delta H_{11}^{\ddagger} \quad (13)$$

$$\Delta S_{app}^{\ddagger} = \Delta S_{10}^{\circ} + \Delta S_{11}^{\ddagger} \quad (14)$$

Since the corresponding entropy terms are both expected to be negative, $\Delta S_{app}^{\ddagger}$ (14) usually has appreciable negative values which results in $\Delta G_{app}^{\ddagger}$ with positive values and the reactions sometimes are relatively slow.

General reaction scheme (10)+(11) has been implicated in a number of cases. The activation enthalpies are found to be significantly smaller than those expected for reactions controlled by translational diffusion. Well characterized examples include the dimerization of phenoxy radicals²⁰⁻²³ as well as nitroxide radicals,²⁴ the proton transfer between 2,4-dinitrophenyl and aliphatic tertiary amines,²⁵ several photochemical reactions,²⁶⁻²⁸ an example of the Diels-Alder reaction²⁹ and the reaction of methyl phenyl ketene.³⁰ Thus, there is ample precedent for this type of behaviour aside from the chemistry of ion radicals. Since ion radical chemistry abounds with examples of coupled equilibria^{31,32} it is very likely that many more examples of negative activation enthalpies will be found upon examinations of the temperature dependence of the reaction kinetics.

EXPERIMENTAL

The cells, electrodes, instruments and data handling procedures were the same as used in other papers in this series.¹⁻⁷ Reagent grade MeCN containing the supporting electrolyte (Bu_4NBF_4) was passed through a column containing neutral alumina before use.

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