Mechanisms of the Electrohydrodimerization of Activated Olefins. VII.* The Validity of Rate–Activation Energy Relationships for Dimerization Reactions of Ion Radicals

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Diethyl fumarate (DEF) anion radical undergoes dimerization in wet dimethylformamide (DMF) by a two-step mechanism involving pre-equilibrium (i) and coupling reaction (ii)

$$DEF^{\cdot-}+Z \overset{K_i}{\rightleftarrows} DEF^{\cdot-}/Z \quad (i)$$

$$DEF^{\cdot-}/Z+DEF^{\cdot-} \xrightarrow{k_{ii}} \text{dimer} \quad (ii)$$

in which Z has been identified as either water or alkali metal cations. The association reaction (i) can have negative $\Delta H°$. Since the rate law for these processes is (iii), the apparent rate constant is equal to $k_{ii}K_i$.

$$\text{Rate} = k_{ii}K_i[DEF^{\cdot-}]^2[Z] \quad (iii)$$

Thus, the apparent activation energies (E_a) reflect the contributions of both k_{ii} and K_i and can be very small and even negative. When Z is H_2O, E_a was observed to be 1.9 kcal/mol $\Delta H_i°$ was found to be −5.9 kcal/mol which results in E_a for reaction (ii) equal to 7.8 kcal/mol. When Z is Na^+, E_a was observed to be 4.1 kcal/mol and K_{ii} at 298 K was estimated to be of the order of 0.2 M^{-1} or less giving a minimum estimate of k_{ii} to be 10^7 $M^{-1}s^{-1}$. A maximum value of 10 $M^{-1}s^{-1}$ (at 298 K) was estimated for the rate constant for the dimerization of uncomplexed $DEF^{\cdot-}$ under the reaction conditions. Assuming that the entropy factors for the latter reaction are similar to reaction (ii) leads to estimations of E_a for the dimerization in the range, 11−12 kcal/mol. It was concluded that anion radical dimerization reactions do not show unusual rate constant–activation energy relationships.

In a preliminary communication of this work,[1] the kinetics of the dimerization of diethyl fumarate (DEF) anion radical in wet dimethylformamide (DMF) were investigated. The reaction was observed to be first order in H_2O and a very small kinetic isotope effect k_H/k_D was observed.

A previous investigation [7] had resulted in a second order rate constants of 44 $M^{-1}s^{-1}$ attributed to reaction (1)

$$2\ DEF^{\cdot-} \xrightarrow{k_1} \text{dimer} \quad (1)$$

with an Arrhenius activation energy (E_a) of about 4 kcal/mol. On the basis of the new kinetic data along with the apparent incompatibility of the rate constant–activation energy data, a two-step mechanism was proposed involving pre-equlibrium (1) followed by coupling reaction (2).

$$DEF^{\cdot-}+H_2O \overset{K_2}{\rightleftarrows} DEF^{\cdot-}/H_2O \quad (2)$$

$$DEF^{\cdot-}/H_2O+DEF^{\cdot-} \xrightarrow{k_3} \text{dimer} \quad (3)$$

Amatore, Pinson and Savéant [8] have commented on this work and imply that this adds little new information to the mechanisms of anion radical dimerization since $DEF^{\cdot-}/H_2O$ is still an anion radical. Therefore, they recommend viewing the

* See Refs. 1−6 for other parts in this series.

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water effect as one of specific solvation as had previously been advocated.[9] The latter view would seem to be totally inconsistent with the reasons for studying the mechanism of a reaction. We find it much more important to identify the various steps in a reaction rather than be satisfied with an overall rate constant for the process. Thus, we consider mechanism (2)+(3) to differ significantly from mechanism (1) with specific solvation of the anion radicals by water.

One of the primary consequences of a pre-equilibrium such as (1) is that the observed activation parameters do not reflect the contributions from a single step and are thus of limited value in discussions of the energetics of the reactions. On the other hand, the observation of unusual effects of the temperature upon observed rate constants can be of importance in assigning mechanisms to reactions. Such studies are common in physical organic chemistry [10] but have been used to a very limited extent in the study of electrode processes. This was recently pointed out and examples were discussed where inverse temperature effects were observed.[12] Savéant and coworkers [8,13] have attacked our use of low activation energies as an indication of complex reaction mechanisms and have implied that we have overlooked classical results of chemical rate theory. We have invoked arguments relating to temperature effects a number of times and thus this issue is of considerable importance to our work. The evidence and conclusions arrived at for a number of processes with unusual temperature behaviour are summarized in Table 1.

In order to gain a better understanding of rate constant–activation energy relationships for ion radical dimerization reactions, two known cases involving pre-equilibria were reinvestigated. The reactions studied were the anion radical water complex reaction (2)+(3) and the ion association reaction (4) and (5)

$$DEF^{\cdot-} + M^{+} \underset{}{\overset{K_4}{\rightleftarrows}} DEF^{\cdot-}/M^{+} \tag{4}$$

$$DEF^{\cdot-}/M^{+} + DEF^{\cdot-} \xrightarrow{k_5} \text{dimer} \tag{5}$$

previously studied in DMF by Hazelrigg and Bard [19] and in DMSO by Ryan and Evans.[20]

RESULTS

The effect of water on the rate of dimerization of diethyl fumarate anion radical. In the preliminary report of this work the water concentration was varied up to 0.55 M in DMF and an approximate first order relationship was observed.[1] Rate

Table 1. Unusual temperature effects reported for electrode processes.

Process	Evidence	Conclusions	Ref.
Dehalodimerization of 4-halo-*N,N*-dimethyl aniline cation radicals	$E_a \sim 0$	Reversible dimerization	13
Deprotonation of hexamethylbenzene cation radicals	Inverse temperature effect $E_a \sim -4$ kcal/mol	Complex kinetic scheme	11
Dimerization of dimethoxystilbene cation radicals	$E_a \sim 0$	Complex mechanism	14
Coupling of 4-methoxybiphenyl cation radicals	$E_a \sim 0$ at low concentration	Complex mechanism	15
Dimerization of 9-substituted anthracene anion radicals	$E_a < 1$ kcal/mol for the 9-nitro derivative	Pre-equilibrium followed by dimer formation	16–17
Dimerization of 9-diazofluorene anion radicals	Non-linear Arrhenius plot, $E_a \sim 2$ kcal/mol	Pre-equilibrium followed by dimer formation	18
Dimerization of *p*-methylbenzylidene malononitrile anion radicals	Concentration dependent E_a as low as 1 kcal/mol	Pre-equilibrium followed by dimer formation	6

Table 2. Effect of water on the dimerization of diethyl fumarate anion radical in DMF.[a]

$[H_2O]$/mM	Lit.[b] $k_{obs}/M^{-1}s^{-1}$	This work $k_{obs}/M^{-1}s^{-1}$	$k^c/M^{-2}s^{-1}$	
139	121	—		
278	242	235	845	
417	349	—		
550	458	412	749	743±13
820		618	754	
1090		817	750	
1355		980	723	
1618		1193	737	
Intercept[d]/$M^{-1}s^{-1}$	11	30		
Corr. coef.[d]	0.9997	0.9995		

[a] Measurements by derivative cyclic voltammetry at a gold electrode at 20.6 °C. [b] The rate constants reported in Ref. 1 are too large by a factor of 1.42. The correct relationship between $v_{1/2}$ and k at 295 °C is $k=4.64\ v_{1/2}/C_A$. [c] Third order rate constants obtained by dividing k_{obs} by the water concentration. [d] From correlation of k_{obs} *vs.* C_{H_2O}.

constants as a function of C_{H_2O} are gathered in Table 2. The data are from this work as well as from Ref. 1 and include C_{H_2O} up to 1.6 M. The observed rate constants (k_{obs}) correlate linearly with C_{H_2O} and give intercepts which should be related to the second order rate constant in the absence of added water. At C_{H_2O} greater than 0.5 M the third order rate constants obtained by dividing k_{obs} by C_{H_2O} were observed to be constant to ±2 % with a value of 743 $M^{-2}s^{-1}$. The extrapolated rate constants C_{H_2O} (added water)=0 correspond to those expected if the residual water introduced in the solvent-electrolyte was 15 (11 $M^{-2}s^{-1}$) and 40 (30 $M^{-2}s^{-1}$) mM assuming all the reaction goes according to mechanism (2)+(3).

The effect of water on the reversible potential for the reduction of diethyl fumarate in DMF. The phase selective second harmonic *a.c.* zero crossing potentials (E_{zc}) gathered in Table 3 were obtained on a solution of DEF (0.1 mM) in DMF. The reason for the low concentration of DEF was to diminish the effect of the second order reaction of the anion radical on the electrode potential measurements. Measurements were made at frequencies of 100 and 300 Hz. Any kinetic complications would cause E_{zc} at the two frequencies to differ by a degree depending upon the rate of the reaction. At all C_{H_2O} the two E_{zc} are within 0.5 mV of each other. This suffices to show that the potentials listed are for the reversible charge transfer (6).

$$\mathrm{DEF}+e^- \underset{}{\overset{E_{rev}}{\rightleftharpoons}} \mathrm{DEF}^{\cdot -} \quad (6)$$

At C_{H_2O} of 0.14 M or greater, correlation of ΔE_{rev} *vs.* C_{H_2O} resulted in a correlation coefficient of 0.9998 and an intercept of −34 mM. After adding 34 mM to all C_{H_2O}, linear regression over all of the data (including the "dry" entry) resulted in a correlation coefficient of 0.9999 with an intercept of 3.7 mM. Finally, a correlation assuming the "dry" solution to be 30 mM in water and adding 30 mM to all C_{H_2O} gave a correlation coefficient of 0.9999 and an intercept of only −0.3 mM. From this it can be concluded that the residual water introduced in the solvent-electrolyte was present at a concentration of about 30 mM for the experiments described in Table 3. If the association of $DEF^{\cdot -}$ with H_2O can be described by equilibrium (7), the shift in E_{rev} with increasing C_{H_2O} is related to K_7 by eqn. (8).

$$\mathrm{DEF}^{\cdot -}+\mathrm{m}\ H_2O \overset{K_7}{\rightleftharpoons} \mathrm{DEF}^{\cdot -}/(H_2O)_m \quad (7)$$

$$\Delta E_{rev} = (RT/F)\ \ln\,(1+K_7 C_{H_2O}{}^m) \quad (8)$$

The last column in Table 3 shows that the data fit eqn. (8) for $m=1$ reasonably well and omitting the values for the two highest water concentrations results in a value for K_7 of 0.57±0.07 M^{-1}. The increasing trend at the higher water concentration may be due to contributions where $m=2$.

Table 3. The effect of water concentration in DMF on the reversible potential for the reduction of diethyl fumarate.[a]

$[H_2O]$/mM	$-E_{zc}$(100 Hz) [b]	$-E_{zc}$(300 Hz) [b]	ΔE_{rev}/mV	K^d/M^{-1}
Over Al_2O_3	342.98(0.08)	342.72(0.00)	0	—
"Dry" [c]	342.57(0.08)	342.15(0.00)	0.49	0.66
28	342.12(0.08)	341.97(0.00)	0.74	0.52
70	341.66(0.10)	341.66(0.10)	1.20	0.49
139	340.76(0.10)	340.46(0.00)	2.24	0.55
278	338.84(0.10)	338.96(0.18)	3.95	0.55
550	335.01(0.00)	334.63(0.13)	8.03	0.65
1090	327.56(0.10)	327.82(0.25)	15.2	0.74
2020	315.26(0.00)	315.78(0.08)	27.3	0.96

[a] Measurements by phase selective second harmonic a.c. voltammetry at a mercury electrode in solvent containing DEF (0.1 mM) and Bu_4NBF_4 (0.1 M) at 18.9 °C. [b] The quadrature zero current crossing potentials referred to a bias potential of −1.46 V *vs.* Ag/Ag^+ in acetonitrile. The numbers in parentheses refer to the standard deviation in 5 measurements. [c] No added water. [d] The equilibrium constant for the association of $DEF^{\cdot-}$ with water assuming that $[H_2O]$ in the "dry" solution was 30 mM, which was added to all other water concentrations.

The effect of sodium ion on the reversible potential for the reduction of diethyl fumarate in DMF. The data in Table 4 were obtained by phase selective second harmonic *a.c.* voltammetry measurements on a solution containing DEF (0.1 mM) and H_2O (27 mM added) at 18.3 °C. It was only possible to make reliable measurements of C_{NaI} up to 6.6 mM. At C_{NaI} of 13.2 mM the *a.c.* current was greatly diminished and the E_{zc} were not reproducible. At higher C_{NaI} the signal for the quadrature component completely disappeared. This behaviour is most likely due to a phase shift caused by adsorption on the electrode and was not further investigated.

In the C_{NaI} range where E_{rev} measurements were possible, E_{zc} was constant to ±0.2 mV which is about the experimental error in the measurements. The numbers in parentheses in Table 4 refer to the standard deviation in 5 replicate measurements without disturbing the cell. The error becomes larger when the cell is disturbed by the addition of a reagent. The relationship between ΔE_{rev} and K_4 is defined in eqn. (9).

$$\Delta E_{rev} = (RT/F) \ln (1+K_4 C_{Na^+}) \quad (9)$$

Since we conclude that ΔE_{rev} is no greater than 0.2 mV when C_{NaI} is 6.6 mM and assuming that Na^+ is not associated with supporting electrolyte anions as is indicated from other work,[19] we obtain a maximum value of K_4 (where M^+ is Na^+) of about 0.5 M^{-1}.

The reaction order in sodium ion during the dimerization of diethyl fumarate anion radical in DMF. Kinetic measurements were carried out using either derivative cyclic voltammetry (DCV) or double potential step chronoamperometry (DPSC). Second order rate constants obtained at C_{NaI} ranging from 4.2 to 110 mM are summarized in Table 5. Dividing k_{obs} by C_{NaI} gives a third order rate constant which should be independent of C_{NaI} if the reaction is first order in sodium ion. The DCV measurements gave a value of $1.04\pm0.07\times10^6$ $M^{-2}s^{-1}$ while a value of $1.53\pm0.11\times10^6$ $M^{-2}s^{-1}$ was obtained from the

Table 4. The effect of sodium ion concentration on the reversible potential for the reduction of diethyl fumarate in DMF.[a]

[NaI]/mM	$-E_{zc}$(300 Hz) [b]
0	328.1(0.1)
3.3	327.8(0.1)
6.6	328.2(0.1)
13.2	diminished signal [c]

[a] Measurements by phase selective second harmonic *a.c.* voltammetry at a mercury electrode in solvent containing Bu_4NBF_4 (0.1 M), DEF (0.1 mM) and water (27 mM added) at 18.3 °C. [b] Zero current crossing potential of the quadrature component referred to a bias potential of −1.47 V *vs.* Ag/Ag^+ in acetonitrile. The numbers in parentheses refer to the standard deviation in 5 measurements. [c] At this concentration the *a.c.* signal became very small and completely disappeared at higher concentrations.

Table 5. The reaction order in sodium ion in the dimerization of diethyl fumarate anion radical in DMF.[a]

[NaI]/mM	Method [b]	k_{obs}/M^{-1}s^{-1}	$10^{-1}k_{obs}$/[Na$^+$]/M^{-2}s^{-1}
4.18	DCV	4.18×10^3	1.00
8.35	DCV	8.07×10^3	0.967
16.7	DCV	1.66×10^4	0.994
55.0	DCV	6.19×10^4	1.12
110	DCV	1.21×10^5	1.10
			1.04±0.07
16.7	DPSC	2.33×10^4	1.40
55.0	DPSC	8.68×10^4	1.58
110	DPSC	1.61×10^4	1.61
			1.53±0.11

[a] In solvent containing Bu_4NBF_4 (0.1 M), water (70 mM) and DEF (2.0 mM) at 16.3 °C. [b] Measurements by either derivative cyclic voltammetry or double potential step chronoamperometry at an Hg electrode.

DPSC data. The deviations observed are about those expected from experimental error. We can conclude that under the conditions of our measurements, the reaction is first order in sodium ion.

The rate constants obtained by DCV are about 0.67 those from DPSC. We have no explanation for this discrepancy but note that it is not uncommon that absolute values of rate constants obtained by various electrochemical techniques differ somewhat.

Apparent activation energies for the dimerization of diethyl fumarate in DMF. Apparent second order rate constants for the dimerization of DEF$^{\cdot-}$ under various conditions were obtained over temperatures ranging from −6 to 40 °C. Arrhenius activation energies along with k_{298}, apparent second order rate constants at 298 K, obtained from the correlations are summarized in Table 6. The correlation coefficients are for correlation of the rate constants measured at five different temperatures. The point of most interest is that E_a is about 1.9 kcal/mol when H_2O but no metal ions are present, about 4.4 kcal/mol in the presence of Li^+ and 4.1 kcal/mol in the presence of Na^+ ions.

In order to determine the degree of precision in the E_a values, three determinations were carried out by DPSC on the same solution containing DEF (2.0 mM), NaI (16.7 mM) and water (70 mM added). The data are shown in Table 7. The correlations resulted in E_a equal to 4.1±0.1 kcal/mol and k_{298} equal to $2.95\pm0.08\times10^4$ M^{-1}s^{-1}.

Table 6. Apparent activation energies and rate constants for the dimerization of diethyl fumarate anion radical in DMF.[a]

[DEF]/mM	[H_2O]/mM	[M^+]/mM	Method [b]	k_{298}/M^{-1}s^{-1}	E_a/kcal mol^{-1}	r [c]
2.0	1090	0	DCV	1.14×10^3	1.9	0.994
9.6	1090	0	DCV [d]	0.86×10^3	1.8	0.989
2.0	dry [e]	4.7(Li^+)	DPSC	1.88×10^4	4.4	0.997
2.0	dry [e]	11.8(Li^+)	DPSC	4.10×10^4	4.3	0.999
1.9	dry [e]	8.0(Na^+)	DPSC	1.10×10^4	4.0	0.985
1.9	dry [e]	8.0(Na^+)	DCV	7.59×10^3	4.2	1.000
1.9	dry [e]	3.3(Na^+)	DCV	3.12×10^3	3.9	1.000

[a] Measurements at 5 different temperatures ranging from −6 to 40 °C. [b] Derivative cyclic voltammetry (DVC) and double potential step chronoamperometry (DPSC). [c] Correlation coefficient of the Arrhenius plot. [d] At a gold electrode, all other measurements were at mercury electrodes. [e] No added water.

Table 7. Precision of activation energy measurements for the dimerization of diethyl fumarate anion radical in DMF.[a]

Determination [b]	E_a/kcal mol^{-1}	$10^{-4}k_{298}$/M^{-1}s^{-1} [c]
1	4.2	2.86
2	4.0	3.00
3	4.1	2.98
	4.1±0.1	2.95±0.08

[a] In solvent containing Bu_4NBF_4 (0.1 M), water (70 mM added), DEF (2.0 mM) and sodium iodide (16.7 mM). [b] Replicate measurements on the same solution at five temperatures ranging from −6 to 40 °C by DPSC at a mercury electrode. [c] Apparent second order rate constant at 298 K.

Table 9. The effect of temperature on the equilibrium constant for the association of diethyl fumarate anion radical with water in DMF.[a]

T/K	K [b]/M	$-\Delta S°$ [c]/cal K^{-1}mol^{-1}
302.4	0.44	21.1
292.1	0.56(0.01) [d]	21.4
272.9	1.24(0.42) [e]	21.2

[a] Measurements by phase selective second harmonic a.c. voltammetry at 300 Hz and d.c. sweep rate of 40.0 mV/s. [b] Calculated from ΔE_{rev} at water concentrations ranging rom 0.1 to 0.6 M. [c] Calculated using the observed value of $\Delta H°$ equal to −5.9 kcal/mol (correlation coefficient=0.994). [d] Two independent determinations. [e] Four independent determinations.

The effect of water on the rate and activation energy of the anion radical–sodium ion pair reaction. The data in Table 8 were obtained by DCV on solutions containing DEF (2.0 mM) and NaI (8.7 mM). The value of E_a was found to be nearly independent of C_{H_2O} and equal to 3.6±0.2 kcal/mol while a slight trend was found in k_{obs} with increasing water concentration. The column labeled k_{corr} is k_{obs} corrected for the contribution of the water reaction with a second order rate constant of 743 M^{-1}s^{-1} (Table 2). The decreasing trend is quite apparent in k_{corr}. What can be concluded from this data is that the product k_5K_4 decreases slightly with increasing water concentration. It seems likely that K_4 is decreased and k_5 is either unaffected or increased.

A further point concerning the data in Table 8 is that E_a measured by DCV are about 0.5 kcal/mol less than those obtained by DPSC. A possible reason for this is that the DCV data are somewhat more sensitive to uncompensated solution resistance than are the DPSC data. We have observed that some adsorption takes place in the presence of sodium ion (Table 4). This could bring about uncompensated resistance problems and contribute to some error in DCV activation energies. For this reason we regard the DPSC values in Table 7 to be more reliable than those in Table 8.

The thermodynamic parameters for the association of diethyl fumarate anion radical with water. Equilibium constants for reaction (7) where $m=1$ were determined at three temperatures with C_{H_2O} ranging from 0.1 to 0.6 M. The data are summarized in Table 9. Significant variations in the K_7 values were observed at the lowest temperature and 4 independent determinations were made. Correlation of ln K_7 *vs.* T^{-1} resulted in an estimate of −5.9 kcal/mol for $\Delta H°_7$ and a correlation coefficient of 0.994. The last column gives the values of $\Delta S°_7$ and the small degree of variation shows that the data are linearly related.

Table 8. The effect of water concentration on the kinetics of the dimerization of diethyl fumarate anion radical in DMF in the presence of sodium iodide.[a]

$[H_2O]$/mM	E_a/kcal mol^{-1}	$10^{-4}k_{obs}$/M^{-1}s^{-1}	$10^{-4}k_{corr.}$ [b]/M^{-1}s^{-1}
0	3.5	1.11	1.11
69.5	3.8	1.02	1.02
139	3.2	0.994	0.984
278	3.4	1.020	1.000
550	3.7	0.973	0.932
1090	3.7	0.955	0.874

[a] Measurements by DCV in solvent containing Bu_4NBF_4 (0.1 M), sodium iodide (8.7 mM) and DEF (2.0 mM) at a mercury electrode. Data at five temperatures ranging from −6 to 40 °C. [b] k_{obs} (at 298 K) corrected by subtracting $743C_{H_2O}$.

DISCUSSION

For the general case of an anion radical dimerization consisting of pre-equilibrium (10) followed by coupling reaction (11),

$$A^{\cdot-}+Z \overset{K_{10}}{\rightleftharpoons} A^{\cdot-}/Z \quad (10)$$

$$A^{\cdot-}/Z+A^{\cdot-} \overset{k_{11}}{\longrightarrow} \text{dimer} \quad (11)$$

the apparent rate constants and activation energies are expected to depend strongly on K_{10}. If K_{10} is much greater than 1 and Z is in excess, essentially all of $A^{\cdot-}$ will exist as $A^{\cdot-}/Z$ in solution and both the rate of the reaction and the apparent E_a will be independent of K_{10} and C_Z. Under these circumstances reaction (11) would probably be insignificant compared to the dimerization of $A^{\cdot-}/Z$. (12).

$$2\ A^{\cdot-}/Z \overset{k_{12}}{\longrightarrow} \text{dimer} \quad (12)$$

On the other hand, if K_{10} and C_Z are sufficiently small that $A^{\cdot-}$ is the predominant species in solution the rate law will be (13)

$$\text{Rate}_{10,11} = k_{11}K_{10}C_{A^{\cdot-}}{}^{2}C_Z \quad (13)$$

and the observed kinetic parameters will depend upon both k_{11} and K_{10}. The apparent activation energy will depend not only on E_a for (11) but also on ΔH° for (10). Association reactons such as (10) are usually exothermic as has been well established for ion pair formation between alkali metal cations and anion radicals in ethereal solvents.[21] The exothermicity of such interactions is expected to increase with increasing solvent polarity.[21] Thus, it is reasonable to expect ΔH°_2 (complexing with water) and ΔH°_4 (ion pairing with Na^+ and Li^+) to be negative for the reactions of $DEF^{\cdot-}$ in DMF.

Before discussing the kinetic parameters for the two reactions it is necessary to establish that the observed rate laws conform to the pre-equilibrium mechanisms. That the dimerizations are clearly second order in $DEF^{\cdot-}$ has been firmly established in the presence of water [1,7] and in the presence of alkali metal ions.[19] It is evident from the data in Table 2 that the reaction is first order in water in the absence of alkali metal ions. Thus, the rate law in the presence of water is (14).

$$\text{Rate}_{2,3} = k_3K_3C_{DEF^{\cdot-}}{}^{2}C_{H_2O} \quad (14)$$

Since our reaction order data for Li^+ is limited to evaluation from only two rate constants we will limit our discussion of reactions (4)+(5) to the case where M^+ is sodium ion. The data in Table 5 show that the reaction order is 1.04±0.07 up to C_{Na^+} as great as 0.11 M. The rate law in the presence of Na^+ is (15).

$$\text{Rate}_{4,5} = k_5K_4C_{DEF^{\cdot-}}{}^{2}C_{Na^+} \quad (15)$$

Hazelrigg and Bard [19] found a small increasing trend in the observed rate constants with increasing C_{NaI} and attributed this to the contribution of reaction (16).

$$2\ DEF^{\cdot-}/Na^+ \overset{k_{16}}{\longrightarrow} \text{dimer} \quad (16)$$

However, electrode filming limited their studies to C_{NaI} up to 8 mM. The reason that we were able to use much higher C_{NaI} is apparently that our solutions contained more water (C_{H_2O},added=70 mM). In any event, it is clear from the data in Table 5 that there is either no or negligible contribution from reacton (16) under our conditions. It could be that K_4 is sufficiently reduced by the inclusion of water to preclude the occurrence of reaction (16).

The most important consequence of the observation that the reactions follow rate laws (14) and (15) is that the observed E_a will be minimum values since both ΔH°_2 and ΔH°_4 are expected to be negative. Indeed, ΔH°_2 was observed to be equal to −5.9 kcal/mol (Table 9). In the case of reaction (4) no shift in E_{rev} could be found at sodium ion concentrations where meaningful measurements could be carried out (Table 4) and K_4 at 292 K was estimated to be less than 0.5 M^{-1}.

The values of E_a observed were 1.9 and 4.1 kcal/mol for reactions (2)+(3) and (4)+(5), respectively. At 298 K, K_2 is of the order of 0.5. The apparent value of k_3K_2 was estimated to be equal to 743 $M^{-2}s^{-1}$ (Table 2) which then results in a value of 1500 $M^{-1}s^{-1}$ for k_3. The activation energy for reaction (3) can be estimated by substracting the contribution of ΔH°_2, *i.e.* −5.9 kcal/mol, from the apparent E_a which results in a value of 7.8 kcal/mol. The value of k_5K_4 at 298 K can be derived from the data in Table 5 and is equal to 1.8×10^6 $M^{-2}s^{-1}$ at C_{H_2O} of 70 mM (added). Since K_4 was estimated to be <0.5 M^{-1} at C_{H_2O} of 27 mM (added) and it is expected to be even lower at higher C_{H_2O}, an estimate of 0.2 M^{-1} would not be unreasonable. Thus, k_5 is most likely of the order of 10^7 $M^{-1}s^{-1}$ or greater and it is surely greater than 5×10^6 $M^{-1}s^{-1}$ under the conditions of the measurements.

The residual water in the DMF–Bu_4NBF_4 solvent-electrolyte system was estimated to be equal to 30 mM (Results section) and the apparent rate constant in the absence of added water (and alkali metal ions) was estimated by extrapolation to be 30 $M^{-1}s^{-1}$ in this work (Table 2) while k_3K_2 was equal to 743 $M^{-2}s^{-1}$. This implies that if reaction (1) takes place at all under the conditions of this study, k_1 is equal to or less than about 10 $M^{-1}s^{-1}$. Why are reactions (3) and (5) so much more favorable than reaction (1)? The obvious explanation is that the complexing of $DEF^{\cdot-}$ with water (2), most likely by hydrogen bonding, or pairing with alkali metal ions (4) reduces the charge repulsion in the dimer forming transition states and results in decreases in the activation energies of reactions (3) and (5) relative to reaction (1). The degree of the reduction of charge repulsion must depend upon how effectively the charge in $DEF^{\cdot-}$ is neutralized by the complex formation. Clearly, ion pairing must be more effective in charge neutralization than is hydrogen bonding. Therefore, it appears safe to conclude that $(E_a)_1>(E_a)_3>(E_a)_5$ where the subscripts refer to the eqn. numbers for the reactions.

The value of $(E_a)_3$ was determined to be 7.8 kcal/mol. From this value and the estimated value of k_3 at 298 K, *i.e.* 1500 $M^{-1}s^{-1}$, the Arrhenius log A [eqn. (17)]

$$\log k = \log A - E_a/(\ln 10RT) \qquad (17)$$

can be estimated to be 9. Assuming the same log A and that k_1 is equal to 10 $M^{-1}s^{-1}$ at 298 K, we arrive at a value of 10.9 kcal/mol for reaction (1). A conservative estimate of $(E_a)_5$ can be taken to be 4.1 kcal/mol. This is surely a minimum value since ΔH°_4 is most likely negative and a greater apparent E_a (4.4 kcal/mol) was obtained when M^+ was Li^+. This conservative value of $(E_a)_5$ can be used to get another estimate of $(E_a)_1$. Assuming a value of 10^7 $M^{-1}s^{-1}$ for k and 4.1 kcal/mol for E_a results in log A equal to 10. This value of log A then results in an estimate of 12.3 kcal/mol for $(E_a)_1$. Accordingly, it is reasonable to conclude that $(E_a)_1$ probably falls somewhere in the range between 11 and 12 kcal/mol.

From the data discussed in the previous paragraphs it is obvious that the dimerization reactions of $DEF^{\cdot-}$ in DMF have activation parameters in the range expected for normal second order reactions. There does not appear to be anything unusual about the rate constant–activation energy relationship for these reactions. Furthermore, there does not appear to be any reason to believe that the situation should differ for other related dimerizations of anion radicals having similar structural features. The use of the apparent activation energy as a guide in proposing complex reaction mechanisms (Table 1) [6,11,13–18] appears to be a safe procedure in ion radical reactions as well in other second order reactions.[10] The comments of Savéant [12] as well as those by Amatore, Pinson and Savéant regarding our use of low activation energies as well as the implication [8] that we have overlooked classical results of chemical rate theory appear to be without justification.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures were those described earlier.[22] Reagent grade DMF containing the supporting electrolyte (Bu_4NBF_4) was passed through a column containing neutral alumina before use. Reagent grade DEF was used without further purification. Double potential step chronoamperometry was carried out by potential steps from about 300 mV less negative than E_{rev} to about 300 mV more negative at about 50 s intervals between measurements. Derivative cyclic voltammetry experiments were carried out as previously described.[23]

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