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Are Low or Negative Activation Enthalpies Consistent with the Alleged One Step Mechanism for the Dimerization of 9-Substituted Anthracene Anion Radicals?

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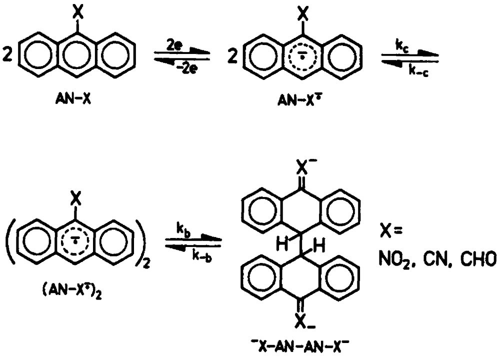
9-Cyano- and 9-nitroanthracene anion radicals undergo dimerization in DMF and DMSO without the interference of acetic acid at concentrations up to about 0.1 M. This allows for the study of the dimerization mechanisms under conditions where the reactions are irreversible. Detailed comparisons of derivative cyclic voltammetric and double potential step chronoamperometric experimental and theoretical data showed the data to fit the dimerization mechanisms, either a simple one step or one involving an association of two anion radicals before bonding occurs. Water at concentrations below about 0.2 M was observed to have a negligible effect on the reaction rates and a competing mechanism becomes significant at higher [H_2O]. Very low enthalpies of activation (1.2 and −0.2 kcal/mol) were observed for the reactions of 9-cyano- and 9-nitroanthracene anion radicals, respectively. The data are discussed in terms of a two step mechanism involving first a reversible association of two anion radicals before the bond forming reaction. The conclusions are compared with current thought in reactive intermediate chemistry where low and negative activation enthalpies are frequently observed.

We recently arrived at the following conclusions,[1] based upon kinetic studies of the *reversible* dimerization of 9-substituted anthracene anion radicals. "Since the only species that we have been able to identify by the voltammetric and kinetic studies involved in the anion radical–dimer dianion equilibria are the ions, we find no alternative than to postulate that the reactions involve two coupled equilibria. The first (Scheme 1) could be the formation of a complex involving two anion radicals which are not covalently bonded to each other and the second involves the reversible bond formation".



Scheme 1.

Amatore, Pinson and Savéant [2] reinvestigated the reactions of 9-cyanoanthracene anion radical and presented a critique of our work. Their conclusions were that a simple dimerization mechanism (1) is followed and that the experimental data, theirs *as well as ours,* are compatible with theoretical data assuming that model. Our conclusions were attributed to artefacts in the kinetic treatment and to the neglect of

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results from classical chemical kinetics. Comments were also made [2,3] concerning related work.[4–6]

$$2\ \mathrm{AN{-}X}^{\cdot-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^{-}\mathrm{X{-}AN{-}AN{-}X}^{-} \qquad (1)$$

A number of comments are in order at the outset regarding the method in which Amatore, Pinson and Savéant [2] have disputed the mechanism that we proposed.[1] Their case lies entirely in the fact that experimental data can be fitted to theoretical data for mechanism (1). What they *do not* consider is that theoretical data are not unique for a particular reaction mechanism and fit equally well for another mechanism giving an identical rate law. The rate law for reaction (1) is (2). This is identical to that for the mechanism in Scheme 1 with the exception that the constants have different meanings as is evident from rate law (3).

$$\mathrm{Rate} = k_1 C^2_{\mathrm{AN\text{-}X}^{\cdot-}} - k_{-1} C_{(\mathrm{X\text{-}AN\text{-}AN\text{-}X})^{2-}} \qquad (2)$$

$$\mathrm{Rate} = k_b K_c C^2_{\mathrm{AN\text{-}X}^{\cdot-}} - k_{-b} C_{(\mathrm{X\text{-}AN\text{-}AN\text{-}X})^{2-}} \qquad (3)$$

Therefore, theoretical working curves are not capable of distinguishing between the two possibilities. The latter should have been emphasized, but was not even mentioned. Because the two mechanisms are indistinguishable from the kinetic point of view some other evidence must be relied upon. We concluded that the apparent activation energies for the reactions were much lower than expected and in the case of $\mathrm{AN{-}NO_2}^{\cdot-}$ there may even be an inverse temperature effect.[1] Amatore, Pinson and Savéant [2] discuss only the $\mathrm{AN{-}CN}^{\cdot-}$ case which we found to have the highest activation energy and they conclude that this is consistent with reaction (1). They do not mention the $\mathrm{AN{-}NO_2}^{\cdot-}$ results which were our strongest point of evidence regarding activation energies. They claim that one of our arguments against the simple one step mechanism was that the Arrhenius pre-exponential factor for the reaction of $\mathrm{AN{-}CN}^{\cdot-}$ was much smaller than the standard collision frequency. The Arrhenius A factor was *not* evaluated in our work.[1] In fact, we did not discuss the possible significance of the A factors for any of the compounds in our study. The A factors that can be calculated from our data [1] (Table 1) are *not* particularly small when compared to values which have been reported for a number of similar reactions in solution.[7] Here we would like to emphasize that in solution the collision process may differ considerably from that in the gas-phase and the use of an A factor based on the collision theory for bimolecular gas-phase reactions as a standard for data obtained in solution is highly questionable.[8] In this context it should also be stressed that because of the accumulative nature of errors, the evaluation of A factors is, as a rule, encumbered with a high degree of uncertainty. For these reasons, along with the fact that the mechanism must be known with certainty before the A factor has significance, we have not based our arguments on the latter. Furthermore, it is surely not justifiable to base mechanistic conclusions on a single A value close to $10^9\ \mathrm{M^{-1}\ s^{-1}}$ as was done.[2]

In this paper, we show that the reactions can be studied without the complications of the reverse

Table 1. Summary of rate constants and activation parameters for the dimerization of 9-substituted anthracene anion radicals in aprotic solvents.

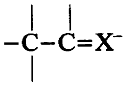
Compound Data from Solvent	9-Cyano Ref. 1 DMF	9-Cyano Ref. 2 DMSO	9-Formyl Ref. 1 DMF	9-Nitro Ref. 1 DMF
$k/\mathrm{M^{-1}\ s^{-1}}$	$1.3 \cdot 10^5$	$1.9 \cdot 10^5$ [a]	$3.1 \cdot 10^5$	$1.6 \cdot 10^6$
$T/^\circ\mathrm{C}$	22	20.5	22	22
$E_a/\mathrm{kcal\ mol^{-1}}$	4.2	4.6	3.2	<1.8 [b,c]
$\Delta H^{\ddagger}/\mathrm{kcal\ mol^{-1}}$	3.6 [c]	4.0 [c]	2.6 [c]	<1.2 [b,c]
$A/\mathrm{M^{-1}\ s^{-1}}$	$2 \cdot 10^8$ [c]	$7.9 \cdot 10^8$	$<3 \cdot 10^7$ [b,c]	
$\Delta S^{\ddagger}/\mathrm{cal\ K^{-1}\ mol^{-1}}$	-23 [c]	-21 [c]	-25 [c]	<-26 [b,c]

[a] k_1. [b] Estimated maximum value from a non-linear Arrhenius plot. [c] Calculated from the data in Refs. 1 and 2.

reactions by having acetic acid present to rapidly protonate the dianions. We support our proposal of a two step mechanism with additional experimental data and show how it is consistent with other recent discussions on similar behaviour observed in reactive intermediate chemistry.

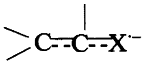
RESULTS AND DISCUSSION

The effect of acetic acid on the dimerization. It has recently been shown [9,10] that some dimerization reactions of anion radicals are kinetically unaffected by the presence of acetic acid in low concentrations. In general, anions with structural element *1* will be more basic and protonated more rapidly than the corresponding anion radical with structural element *2*. This is the situation in



$-\overset{|}{\underset{|}{C}}-\overset{|}{C}=X^-$

1



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such reactions as protonation or dimerization of anion radicals. We have employed these observations to design kinetic experiments under conditions that the dimerization reactions of $AN-X^{\cdot-}$ are irreversible. Under these conditions the last terms in rate laws (2) and (3), due to dissociation of the dimers, are insignificant due to the rapid protonation of the dimer dianions.

The data in Table 2 show the effect of acetic acid concentration on the apparent rate constants for the dimerization of $AN-CN^{\cdot-}$ in DMF at 20.6 °C. The point of importance is that the rate constant is independent, $1.95(\pm 0.13)\times 10^5$ M^{-1} s^{-1}, of the acetic acid concentration up to 40 mM. The rate constant measured by double potential step chronoamperometry (DPSC) [11] is slightly larger than the one we reported earlier,[1] 1.32×10^5 M^{-1} s^{-1}, based on derivative cyclic voltammetry (DCV) studies. A comparable set of experiments indicated that the rate constant for dimerization of $AN-NO_2^{\cdot-}$ is equal to 2.3×10^6 M^{-1} s^{-1} as compared to 1.6×10^6 M^{-1} s^{-1} in the absence of acetic acid. If these small differences are real, the lower values in the absence of the acid could reflect the contribution of the dissociation of the dimer dianions. That the influence of the dissociations is small is also illustrated by the data in Table 1, which summarizes the results from previous work.[1,2] Only in the evaluation of the data reported in Ref. 2 was the contribution from the dissociation taken into account. In spite of this, the data from the two independent studies are almost identical. The lack of influence of the dissociation on observed rate constants is even more clearly brought out by the data in Tables 7 and 8 discussed later.

It was not only necessary to show that the reaction rates for the dimerizations are essentially independent of the acetic acid concentration but also that the reactions remain second order in anion radical as had been demonstrated earlier in the absence of acid.[1] The data in Tables 3 and 4 serve this purpose. The data for $AN-CN^{\cdot-}$ were

Table 2. The effect of acetic acid concentration on the rate of dimerization of 9-cyanoanthracene anion radical.[a]

C_{HOAc}/mM	$\tau_{1/2}$ [b]/ms	k [c]/10^5 M^{-1} s^{-1}
8	7.76	2.14
12	8.95	1.85
20	8.76	1.89
40	8.71	1.91
		Av. 1.95 (0.13)

[a] Measurements by DPSC in DMF containing Bu_4NBF_4 (0.1 M) at 20.6 °C. [b] Pulse width. [c] Rate constant assuming the simple dimerization mechanism.

Table 3. Reaction order study of the dimerization of 9-cyanoanthracene anion radical in the presence of acetic acid.[a]

C_{AN-CN}/mM	T/°C	$\tau_{1/2}$ [b]/ms	k [c]/10^5 M^{-1} s^{-1}
0.5	30.0	8.85	1.88
1.0	30.0	4.86	1.71
2.0	30.0	2.48	1.67
			Av. 1.78 (0.11)
0.5	−29.8	20.6	0.806
1.0	−29.8	11.1	0.748
2.0	−29.8	5.61	0.740
			Av. 0.765 (0.036)

[a] Measurements by DPSC in DMF containing Bu_4NBF_4 (0.1 M) and acetic acid (0.004 M). [b] Pulse width. [c] Rate constant assuming the simple dimerization mechanism.

Table 4. Reaction order study of the dimerization of 9-nitroanthracene anion radical in the presence of acetic acid.[a]

$C_{\mathrm{AN\text{-}NO_2}}$/mM	T/°C	$v_{1/2}{}^{b}$/V s^{-1}	$k^{c}/10^{6}$ M^{-1} s^{-1}
0.1	39.9	50.3	2.19
0.2	39.9	99.0	2.15
0.1	28.8	50.0	2.26
0.2	28.8	95.4	2.15
0.1	10.4	49.7	2.39
0.2	10.4	95.3	2.29
0.1	−0.6	44.5	2.22
0.2	−0.6	80.5	2.01

[a] Measurements by DCV in DMF containing Bu_4NBF_4 (0.1 M) and acetic acid (0.004 M). [b] Sweep rate. [c] Rate constant assuming the simple dimerization mechanism.

obtained by DPSC in the concentration range, 0.50 to 2.00 mM, at two widely separated temperatures, −30 and +30 °C. The apparent rate constants were constant to ±6 % indicating a good fit to second order kinetics. The faster dimerization of $\mathrm{AN{-}NO_2}^{\cdot -}$ was studied by DCV at lower concentrations, 0.1 and 0.2 mM. Because of the low concentrations necessary to hold the rate low enough to make measurements it was not possible to get DPSC data in this case. Apparent rate constants were measured at four temperatures and at each temperature were found to vary by less than ±10 %, again showing a very good fit to second order kinetics.

Table 5. Normalized DPSC working curve analysis of the dimerization of 9-cyanoanthracene anion radical.[a]

R_I	$(kC_\mathrm{A}\tau)_\mathrm{theory}$	$(yC_\mathrm{A}\tau)^{b}_\mathrm{exp}$	$(yC_\mathrm{A}\tau)^{c}_\mathrm{exp}$
0.80	0.20	0.21	0.20
0.75	0.26	0.27	0.27
0.70	0.35	0.35	0.35
0.65	0.43	0.43	0.43
0.60	0.54	0.54	0.55
0.55	0.66	0.67	0.67
0.50	0.83	0.83	0.83
0.45	1.03	1.06	1.03
0.40	1.26	1.30	1.30
0.35	1.58	1.63	1.70
0.30	2.07	2.08	2.12
0.25	2.67	2.73	2.66
$m_1=$		0.97	1.00
$m_2=$		1.00	1.01
$m_\mathrm{T}=$		1.00	1.01

[a] Measurements in DMF containing Bu_4NBF_4 (0.1 M) and acetic acid (0.004 M). $C_{\mathrm{AN\text{-}CN}}$=0.5 mM. [b,c] Two independent data sets.

Thus, we conclude that the dimerization of the anion radicals are unaffected by the presence of low concentrations of acetic acid. In order to test for reversibility, experiments were conducted by DCV at low sweep rates in the manner described earlier.[1] In these cases, the derivative peak current ratio decreased with decreasing v (voltage sweep rate) in the manner expected for an irreversible reaction of the anion radicals. This is in contrast to the opposite behaviour observed in the absence of acetic acid. Therefore, in the presence of the acid the dissociation of the dimer dianion can be neglected. This point will be discussed in more detail in the next section.

Comparison of experimental data for the dimerization reactions to theoretical data. Experimental DPSC data for the dimerization of AN−CN anion radical are compared to theoretical data for irreversible dimerization in Table 5. As mentioned earlier, a fit of experimental and theoretical data in this case does not differentiate between the two mechanisms in question. However, a comparison of the data does give a measure of the compatibility of the experimental data to the mechanisms. The method used for the comparison is that recently reported.[12] For the second order dimerization mechanism the basis of the method is eqn. (4)

$$(yC_\mathrm{A}\tau)_{R_\mathrm{I}} = (kC_\mathrm{A}\tau)_{R_\mathrm{I}} \tag{4}$$

which states that at any particular value of R_I, the normalized current ratio, the pulse width τ multiplied by the substrate concentration C_A and a constant y is equal to the theoretical value of $kC_\mathrm{A}\tau$ for a perfect fit of experimental to theoretical data. If the theoretical data apply to the mechanism being investigated, y is equal to the rate constant k for the process. We evaluated y by assuming relationship (4) when R_I is equal to 0.50 and then calculated $yC_\mathrm{A}\tau$ for each value of R_I given in Table 5. The next step in the analysis involves evaluating three linear regression slopes, in this case m_1 (R_I=0.80−0.50), m_2 (R_I=0.50−0.25) and m_T (R_I=0.80−0.25). For a fit of experimental and theoretical data, $m_1=m_2=m_T$=1.00. In the two independent sets of data we observed 0.97, 1.00, 1.00 and 1.00, 1.01, and 1.01 for the three slopes. This represents an acceptable fit of data for the dimerization mechanisms. Data at τ less than 2 ms were observed to deviate from the theoretical values and were not included in the correlations. We do not consider this deviation serious since low C_A (0.5 mM) were involved which can give rise to interference by the double layer charging process at short times. Theoretical data for different mechanisms usually do not differ much for high values of R_I. The most significant deviations are expected at long times and would be reflected in m_2.

The data in Table 6 are for a comparable DCV analysis of the dimerization of AN−NO$_2^{\cdot-}$ in DMF both in the presence (4 mM) and absence of acetic acid. In both cases m_1 (R'_I=0.70−0.50) and a slope encompassing R'_I from 0.70 to 0.40 were reasonably close to unity, 1.01 and 1.04 (in the presence of HOAc) and 0.97 and 1.07 (in the absence of HOAc). At lower R'_I yC_A/a where a is Fv/RT deviated significantly from the theoretical values of kC_A/a. Analysis of the AN−CN$^{\cdot-}$ dimerization using CV and a concentration of 0.5 mM gave similar results. The data fit the working curve at short times, *i.e.* down to R'_I of about 0.4, but deviate at long times. We do not have a good explanation of this behaviour but have good reason to believe that it is not due to a deviation from the reaction mechanism at long times since an excellent fit of data to the DPSC working curve was observed under comparable conditions for AN−CN$^{\cdot-}$ as demonstrated in Table 5. Any electrode surface complicatons would influence the data most at long times and low concentrations. The fact that the data for the two experiments in Table 6 are identical within experimental error illustrates that the dissociation of the dimer dianion does not influence the data even when acetic acid is not present.

What we can conclude from the data in Tables 5 and 6 is that in the presence of small amounts of acetic acid experimental data for the reactions of both AN−CN$^{\cdot-}$ and AN−NO$_2^{\cdot-}$ are consistent with theoretical data for the dimerization mechanisms.

The role of water in the dimerization of 9-cyanoanthracene anion radical in DMF and DMSO. The effect of added water on the apparent rate constants for the dimerization of AN−CN$^{\cdot-}$ in the absence and the presence of HOAc (4.4 mM) in DMF and DMSO is shown by the data in Tables 7 and 8, respectively. In all cases, the data show that water has a negligible effect at concentrations lower than about 0.2 M. The data were treated in the same manner as in a recent study on the dimerization of benzaldehyde anion radical in aqueous ethanol.[13] Since the reaction is second order in anion radical regardless of the water concentration, the apparent rate constant k_{app} must consist of a term for the reaction not involving water (k_0) and that involving water, k_W. If the latter is first order in water, k_{app} is described by eqn. (5).

$$k_{app} = k_0 + k_W[H_2O] \qquad (5)$$

If (5) is an adequate description of k_{app}, dividing the $k_W[H_2O]$ term by the concentration of added water should result in a constant which is the third order rate constant for the reaction second order in AN−CN$^{\cdot-}$ and first order in water. On the other hand, if there is any contribution from a reaction second order in water, k_W will not be a constant and will increase with increasing [H$_2$O]. In DMF rate constants were determined at [H$_2$O] as great as 2.5 M while

Table 6. Normalized DCV working curve analysis of the dimerization of the 9-nitroanthracene anion radical.[a]

R'_I	$(kC_A/a)_{theory}$	$(yC_A/a)^{b}_{exp}$	$(yC_A/a)^{c}_{exp}$
0.70	0.039	0.036	0.039
0.65	0.048	0.050	0.052
0.60	0.065	0.066	0.067
0.55	0.087	0.087	0.084
0.50	0.118	0.118	0.118
0.45	0.165	0.165	0.162
0.40	0.24	0.25	0.26
0.35	0.38	0.43	0.42
0.30	0.62	0.86	1.01
0.25	1.12	2.48	1.79

[a] The analysis is described in the text. Measurements in DMF containing Bu$_4$NBF$_4$ (0.1 M). [b] C_{AN-NO_2}=0.1 mM, C_{HOAc}=1.6 mM. *c* As *b*, but without HOAc.

Table 7. The effect of water on the rate of dimerization of 9-cyanoanthracene anion radical in DMF.[a]

C_{H_2O}/M	C_{HOAc}/mM	$k^b/10^5$ M^{-1} s^{-1}	$k_W C_{H_2O}/10^5$ M^{-1} s^{-1}	$k_W/10^5$ M^{-2} s^{-1}
0	0	2.00	–	–
0.19	0	2.03	0.03	0.16
0.37	0	2.22	0.22	0.60
0.55	0	2.23	0.23	0.42
0.73	0	2.31	0.31	0.42
1.09	0	2.45	0.45	0.41
				Av. 0.40 (0.16)
0	4.4	2.06	–	–
0.19	4.4	2.16	0.10	0.54
0.37	4.4	2.18	0.12	0.33
0.55	4.4	2.34	0.28	0.51
0.73	4.4	2.35	0.29	0.40
1.09	4.4	2.52	0.46	0.42
1.79	4.4	2.88	0.82	0.46
2.48	4.4	3.20	1.14	0.46
				Av. 0.45 (0.07)

[a] Measurements by DCV in solvent containing Bu_4NBF_4 (0.1 M) and 9-cyanoanthracene (0.50 mM) at a mercury electrode at 19 °C. [b] Apparent rate constant evaluated from the voltage sweep rate necessary for the ratio of the derivative peaks to equal 0.700.

Table 8. The effect of water on the rate of dimerization of 9-cyanoanthracene anion radical in DMSO.[a]

C_{H_2O}/M	C_{HOAc}/mM	$k^b/10^5$ M^{-1} s^{-1}	$k_W C_{H_2O}/10^5$ M^{-1} s^{-1}	$k_W/10^5$ M^{-2} s^{-1}
0	0	2.60	–	–
0.19	0	2.71	0.11	0.59
0.37	0	2.82	0.22	0.60
0.55	0	2.89	0.29	0.53
0.73	0	2.99	0.39	0.53
1.09	0	3.14	0.54	0.50
1.79	0	3.40	0.80	0.45
2.48	0	3.75	1.15	0.46
3.47	0	4.24	1.64	0.47
				Av. 0.52 (0.06)
0	4.4	2.66	–	–
0.19	4.4	2.72	0.06	0.32
0.37	4.4	2.83	0.17	0.46
0.55	4.4	2.84	0.18	0.33
0.73	4.4	2.95	0.29	0.40
1.09	4.4	3.16	0.50	0.46
1.79	4.4	3.54	0.88	0.49
2.48	4.4	3.86	1.20	0.48
3.47	4.4	4.34	1.68	0.48
				Av. 0.43 (0.07)

[a,b] See Table 7.

water concentrations as high as 3.5 M were employed in the experiments in DMSO. The last columns in Tables 7 and 8 give k_W. In all cases, k_W is constant within experimental error and no trends are evident with increasing [H_2O]. Also, all four series of experiments give values of k_W identical within the error limits. The values observed range from 0.40 to 0.52×10^5 M^{-2} s^{-1}. Another interesting feature of the data are that the rate constants obtained are independent of whether or not acetic acid was present in either solvent. The rate constants measured in DMSO are about 30 % larger than those obtained in DMF.

In the course of the rate constant measurements, the peak potential for the reduction of AN–CN was measured at 100 V s^{-1}. At this sweep rate the ratio of the derivative peaks of the cyclic voltammogram was of the order of 0.65–0.85 so that the peak potential measurement at 100 V s^{-1} was very nearly the reversible value. The peak potentials were observed to be independent of [H_2O] to ±1 mV up to about 1 M and then a slight shift in the negative direction was observed at higher concentrations. The latter is most likely due to some adsorption which was not serious enough to hamper the kinetic measurements. Under normal circumstances, phase selective second harmonic a.c. voltammetry is the method of choice for reversible potential measurements.[14] However, in this case the peak potential measurements discussed above appear to be more reliable. This is evident from the data in Table 9 for the potentials measured by phase selective second harmonic a.c. voltammetry. The potentials listed are for the quadrature component and even greater shifts were observed for the in phase component. The data indicate that some adsorption process is causing a phase shift so that the measured potentials are not the reversible values. But since we could not detect any shift in the peak potentials measured at 100 V s^{-1} at [H_2O] less than 1 M, we conclude that the reversible potential is independent of the water concentration. Thus, $AN-CN^{\cdot-}$ *is not specifically solvated by water* in either DMF or DMSO.

Table 9. Phase selective second harmonic *a.c.* reversible potential measurements on the reduction of 9-cyanoanthracene in aqueous DMSO.[a]

C_{H_2O}/M	$-E_{zc}$(300 Hz)[b]/mV	ΔE_{zc}/mV
0	286.4(0.5)	0
0.19	287.4(0.3)	−1.0
0.37	288.8(0.4)	−2.4
0.55	290.1(0.3)	−3.7
0.73	291.7(0.2)	−5.3
1.09	293.2(0.2)	−6.8

[a] In solvent containing Bu_4NBF_4 (0.1 M) and HOAc (4.4 mM). DC voltage sweep rate was 40.0 mV/s. [b] The zero current crossing potentials of the quadrature component referred to a bias potential of −1.273 V *vs.* Ag/Ag^+ in acetonitrile. The numbers in parentheses are the standard deviations in 5 replicate measurements.

The general effect of water then is that at [H_2O] greater than about 0.2 M, a competing mechanism begins to become important. The reaction is second order in $AN-CN^{\cdot-}$ and first order in water. The most likely mechanism is the pre-equilibrium mechanism previously found for the dimerization of diethyl fumarate anion radical.[4,15] In the present case this mechanism consists of equilibrium (6) followed by reaction (7) and is described by rate law (8).

$$AN-CN^{\cdot-}+H_2O \overset{K_6}{\rightleftharpoons} AN-CN^{\cdot-}/H_2O \qquad (6)$$

$$AN-CN^{\cdot-}/H_2O+AN-CN^{\cdot-} \xrightarrow{k_7} \text{dimer} \qquad (7)$$

$$\text{Rate} = k_7K_6[AN-CN^{\cdot-}]^2[H_2O] \qquad (8)$$

Although it would be possible to gain more definitive information about this reaction by carrying out deuterium kinetic isotope effect studies as has been done in related cases,[4,13] this was deemed unnecessary since the reaction only takes place when substantial amounts of water are added which is aside from the conditions of interest to this study.

Amatore, Pinson and Savéant [2] have commented on the pre-equilibrium mechanism [4] and suggest that specific solvation by water is a safer and more general formulation. In fact, more recently the same authors have suggested that the dimerization of $AN-CN^{\cdot-}$ in DMSO in the presence of water involves specific solvation by water and can involve coupling of either one solvated anion radical with an unsolvated one or of two solvated anion radicals.[16] The first possibility is just a restatement of the pre-equilibrium mechanism. The second possibility implies that the reaction should become second order in water at the higher water concentrations where it is alleged to take place. We do not observe this mechanism even when [H_2O] in DMSO is 3.5 M. The fact that k_6 is apparently very small argues that it would not be possible to observe this mechanism under conditions where the measurements can be made.

It is interesting to note that the pre-equilibrium mechanism [4,15] is now being called specific solvation by water.[16] This is admittedly an unimportant point but one that cannot pass without comment. The use of this terminology is meant to imply that this is what was meant by specific solvation in earlier work.[17] Just to set the record straight we quote from the paper discussing the effect of water on the electrodimerization of anion radicals.[17] The following two paragraphs are taken directly from that paper.

"If, thus, $A^{\cdot-}$ is assumed to be solvated and not protonated by the added water, the only possible reaction sequence is: $A+1e^- \rightleftarrows A^{\cdot-}$, $2A^{\cdot-}$ (solvated by water)$\rightarrow D^{2-}$ (rate determining step), $D^{2-}+2\ H_2O \rightarrow DH_2+2\ OH^-$ 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."

In our opinion, this unwillingness to accept that the pre-equilibrium mechanism is distinctly different from what is implied by specific solvation and the preceding paragraphs leads to confusion and does little for the task at hand, *i.e.* to advance the knowledge on how anion radicals couple. An example of the confusion caused is the effect of water on the rate of dimerization of $AN-CN^{\cdot-}$. We have shown that water has a negligible effect at concentrations less than 0.2 M. A different reaction begins to take place at higher [H_2O] which competes with the mechanism that is being examined in drier media. Then we ask the following question. Why add water in the first place? The overall result is that it confuses the entire issue. If the reason to add water is to study the competing reaction, *i.e.* mechanism (6)+(7), AN−CN is a poor choice of substrate since K_6 is so small that it is not detected by voltammetric measurements. A much better case, the dimerization of diethyl fumarate anion radical, has been studied rather thoroughly.[4,15] In this case it was possible to not only determine K for the association reaction but also to evaluate $\Delta H°$.

The effect of [Bu_4N^+] *on the rate of dimerization of* $AN-CN^{\cdot-}$. Our kinetic data for the dimerization of $AN-CN^{\cdot-}$ and $AN-NO_2^{\cdot-}$ suggest a pre-equilibrium mechanism which we have proposed to consist of the reactions in Scheme 1. An alternative possibility, the water complex mechanism (6)+(7), has been ruled out. A third possibility is that the supporting electrolyte cation, Bu_4N^+, pairs with $AN-CN^{\cdot-}$ in a pre-equilibrium (9) before rate determining coupling reaction (10). In order to test for this mechanism, [Bu_4NBF_4] was varied by a factor of 8 in a series of rate measurements on the dimerization of $AN-CN^{\cdot-}$.

$$AN-CN^{\cdot-}+Bu_4N^+ \overset{K_9}{\rightleftarrows} AN-CN^{\cdot-}/Bu_4N^+ \quad (9)$$

$$AN-CN^{\cdot-}/Bu_4N^+ + AN-CN^{\cdot-} \xrightarrow{k_{10}} \text{dimer} \quad (10)$$

The data are summarized in Table 10. The apparent rate constant does depend upon the supporting electrolyte concentration but increases by only 50 % as [Bu_4NBF_4] was increased from 0.025 to 0.20 M. Mechanism (9)+(10) could account for our data if Bu_4NBF_4 was significantly associated in DMF. However, association constants for tetraalkylammonium salts in DMF are too small [18] to account for the data. We think that it is more likely that the increase in rate caused by the increase in the supporting electrolyte concentration is simply a salt effect. The transition state leading to the formation of the dimer dianion is highly polarized and would be

Table 10. The effect of Bu_4N^+ concentration on the rate of dimerization of 9-cyanoanthracene anion radical in DMF.[a]

$C_{Bu_4NBF_4}$/M	$v_{0.7}$/V s^{-1}	$k/10^5$ M^{-1} s^{-1}
0.025	47.1	1.46
0.050	57.4	1.78
0.100	66.8	2.07
0.200	71.6	2.22

[a] Measurements by DCV at 19 °C at a mercury electrode. The difference in switching and reversible potentials was 300 mV.

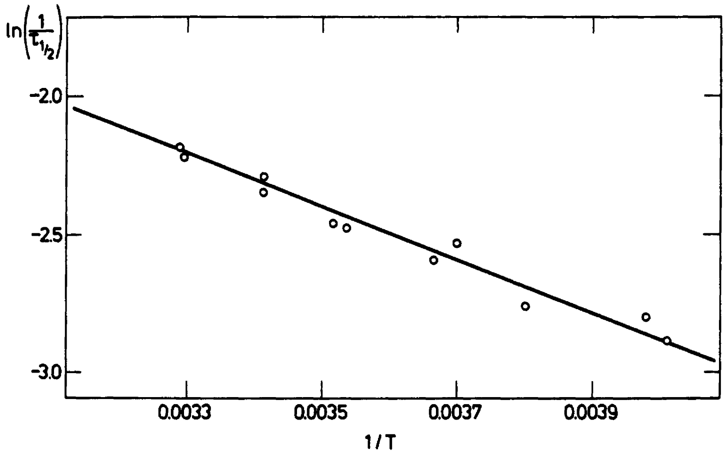

Fig. 1. Arrhenius plot for the dimerization of 9-cyanoanthracene anion radical (0.5 mM) in DMF containing Bu_4NBF_4 (0.1 M) and acetic acid (4 mM).

stabilized by a more polar environment. However, we cannot rule out that mechanism (9)+(10) represents a competing reaction.

The effect of temperature on the kinetics and the mechanistic implications of the results. The kinetics were studied at temperatures ranging from −27 to 31 °C by DPSC for the reaction of $AN-CN^{\cdot-}$ and by DCV for the faster reactions of $AN-NO_2^{\cdot-}$ in DMF containing HOAc. Activation energies were obtained using eqn. (11) for DCV and eqn. (12) for DPSC.[19]

$$\ln (\nu_{1/2}/T) = -E_a/RT + \text{constant} \qquad (11)$$

$$\ln (1/\tau_{1/2}) = -E_a/RT + \text{constant} \qquad (12)$$

The subscripts (1/2) indicate that ν or τ necessary for the normalized current ratios R'_I (DCV) or R_I (DPSC) to equal 0.500 were evaluated at each temperature. It is necessary to divide $\nu_{1/2}$ by T for the activation energy determination since the normalized sweep rate is a ($=F\nu/RT$). The results from these measurements are presented in Figs. 1 and 2. In both cases satisfactory linear relationships according to eqns. (11) and (12) were observed. The activation energies, E_a, and hence enthalpies, $\Delta H^{\ddagger}$,

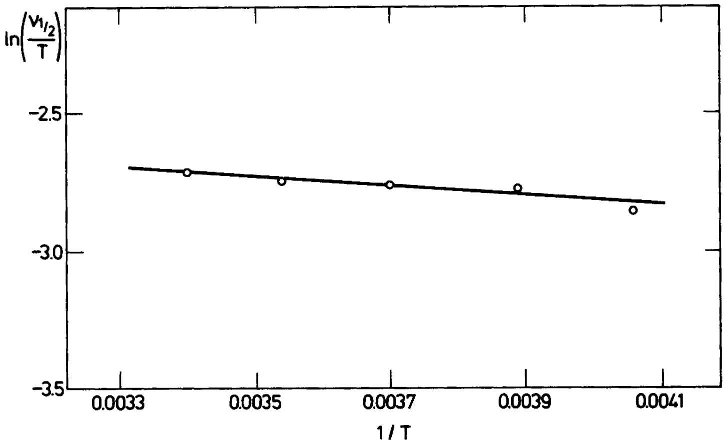

Fig. 2. Arrhenius plot for the dimerization of 9-nitroanthracene anion radical (0.1 mM) in DMF containing Bu_4NBF_4 (0.1 M) and acetic acid (0.8 mM).

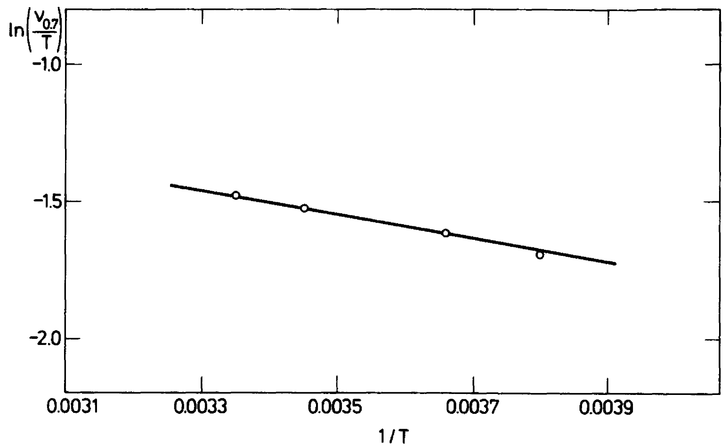

Fig. 3. Arrhenius plot for the dimerization of 9-cyanoanthracene anion radical (0.5 mM) in DMF in the presence of H_2O (0.07 M) and Bu_4NBF_4 (0.1 M).

were calculated from the slopes. The values of the activation enthalpies were found to be 1.2 kcal/mol ($AN-CN^{\cdot-}$) and −0.2 kcal/mol ($AN-NO_2^{\cdot-}$) with activation entropies of −30 cal/K mol in both cases. The values observed in the presence of HOAc are somewhat smaller than those resulting from the measurements in the strictly aprotic solvent.

In order to determine whether or not the presence of acetic acid is responsible for the lower activation energies observed in this study as compared to that reported earlier,[1] we carried out a series of experiments under conditions comparable to those reported in Table 7. Since water does not affect the rate at concentrations lower than about 0.2 M, the experiments were carried out with $[H_2O]$ equal to 0.07 M. To minimize any possible effect of the reversibility of the reaction in the absence of acetic acid, $v_{0.7}$ was taken as the measure of the apparent rate constant. This is equivalent to the measurement of initial rates and involves a time scale about 30 % as long as when $v_{0.5}$ is measured. Measurements were made at temperatures ranging from −10 to 25 °C. The data are illustrated in Fig. 3. The apparent enthalpy of activation was observed to be equal to 0.3 kcal/mol, *i.e.* somewhat smaller that obtained for the data in Fig. 1. Thus, it appears that in the presence of low concentrations of either water or acetic acid the activation enthalpies are very low while the rate of dimerization at room temperature is virtually unaffected.

The important point to be made regarding the activation enthalpies is that they are significantly smaller than those expected for reactions controlled by translational diffusion. Such deviations from "normal behaviour" have been reported in a number of cases including the dimerization of phenoxy radicals [7,20–22] and nitroxide radicals,[23] the proton transfer between 2,4-dinitrophenol and aliphatic tertiary amines,[24] several photochemical reactions,[25–27] an example of the Diels-Alder reaction [28] and the reaction of methyl phenyl ketene with 1-phenyl ethanol.[29] The general conclusion in *all* these chemically very different cases is that the results can only be satisfactorily explained if it is assumed that the reaction in question proceeds through at least one intermediate, in many cases called a complex, which is present in low concentration and in equilibrium with starting material (eqns. (13) and (14)). This mechanism gives rise to rate law (15).

$$\text{A+B (or A)} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} \text{C} \quad (13)$$

$$\text{C} \xrightarrow{k_{14}} \text{D} \quad (14)$$

$$\text{Rate} = \frac{k_{13}k_{14}}{k_{-13}+k_{14}}[\text{A}][\text{B}] \text{ or } \frac{k_{13}k_{14}}{k_{-13}+k_{14}}[\text{A}]^2 \quad (15)$$

Because the heat of formation for the complex, ΔH°_{13}, is a negative term, the overall activation enthalpy, $\Delta H^{\ddagger}$, which is made up of two terms (eqn. (16)), may become very small and even negative.

$$\Delta H^{\ddagger} = \Delta H^\circ_{13} + \Delta H^{\ddagger}_{14} \tag{16}$$

Similarly the activation enthropy, $\Delta S^{\ddagger}$, consists of two terms (eqn. (17)).

$$\Delta S^{\ddagger} = \Delta S^\circ_{13} + \Delta S^{\ddagger}_{14} \tag{17}$$

These are both negative resulting in $\Delta S^{\ddagger}$ values typically in the range -15 to -40 cal/K mol, but values as low as -70 cal/K mol have been reported in special cases.[23,29] As a result of this, $\Delta G^{\ddagger}$ may take appreciable positive values and consequently the reactions appear as relatively slow. The values we find for the activation enthropies, with or without HOAc present, are all between -23 and -30 cal/K mol and thus in excellent agreement with our view on the mechanism, *i.e.* that the reaction passes through an intermediate, or in other words that the potential energy surface for the reaction has at least one energy minimum.[30,31] We do not wish to speculate on the nature or the life-time of these intermediates. However, in the light of the view expressed [3] that the relative slowness of the reactions could be explained, as an alternative to our proposal, by assuming that a large fraction of the collisions between the anion radicals are inefficient and thus not leading to products, we do want to point out an important feature of collisions in solution. Compared to the gas-phase where the life-time of an encounter complex is only that of one collision, an encounter complex in solution may survive as many as 1000 collisions between the reactants before they separate again or go to products, the so-called cage-effect.[8,32-35] The interactions between the molecules in the solvent cage are rather weak and not strictly directional and do not hinder rotational or translational events within the cage, events which finally may lead to the right geometry for bond formation. Whether or not such a complex will manifest itself kinetically as an intermediate is a question of how deep the energy minimum is and the relative importance of the contributions from enthalpy and entropy terms. Obviously we do not believe that all such collisions are efficient in the present case, but the steric requirements for the bond formation are in no way related to the question of the number of elementary steps in the reaction.

Thus, although our experimental results are unusual they are *not* sufficiently peculiar that their interpretation requires that we have to "overlook rather classical results of chemical rate theory".[2] On the contrary. As it is evident from the discussion in the preceding paragraphs our observation of $\Delta H^{\ddagger}$-values significantly smaller than those for diffusion controlled reactions is perfectly compatible with classical rate theory even without the necessity to speculate on the nature of the molecular collisions or to argue by help of non-specific steric factors.[2,3] The way in which the criticism of our work is based on such arguments is reminiscent of the following section from North's book:[8] "One of the most unsatisfactory features of the collision theories of chemical reactions is the so-called steric factor. This factor is incorporated into the rate expression for a chemical reaction in order to include the probability that the orientation of the molecules during a collision may or may not be favourable for chemical reaction to take place. It therefore is very often of an empirical nature, and as such used as a cloak for ignorance in fitting experimentally observed rate constants to so-called "normal theoretical" values".

Comments on the "reaction order" approach. Amatore, Pinson and Savéant [2] imply that the kinetic methods developed in one of our laboratories [36,37] and for simplicity described as the "reaction order" approach have been known for a long time. To substantiate the latter, reference was made to an older paper.[38]

Before rebutting these implications we must examine what is meant by the "reaction order" approach and some of the circumstances which led to its development in the way it is meant to be applied. During the study of two different electrode processes, the oxidation of hexamethylbenzene and 4-bromoanisole in acetonitrile, good fit of experimental data to theoretical working curves for first order processes were observed.[39] In both cases, the rate constants observed were strongly dependent upon the substrate concentrations showing that the fit of experimental and theoretical data was coincidental in both cases. In addition, unusual temperature effects were observed. In fact, apparent negative activation energies of the order of −4 kcal/mol were observed for the hexamethylbenzene and the perdeuterated isomer cation radical reactions. Following this, it was pointed out that apparent activation energies can be derived from experimental voltammetric data without doing any calculations or without being aware of the mechanism of the process in question.[19] The only requirement for the application of this method is that the electrode response can be described by eqn. (18)

$$\text{Observable} = \mathrm{f}(k \cdot \text{Variables}) \qquad (18)$$

in which the Observable is the measured quantity such as the peak current ratio in cyclic voltammetry and the variables are the time of the experiment (sweep rate in CV), concentration, *etc.* Eqn. (18) then is the basis for the "reaction order" approach. The method was amplified [36] and it was shown that it could be used to define the rate law for an unknown process without doing any theoretical calculations. A limitation of the method, which was clearly pointed out,[36] is that the reaction orders in substrate (A) and primary intermediate (B) defined in eqn. (19)

$$A \pm e^- \rightleftharpoons B \qquad (19)$$

are not separable and were expressed as $R_{A/B}$. It was suggested that this uncertainty should be taken into account by examining possible mechanisms with the appropriate combinations of the individual reaction orders R_A and R_B.

Amatore, Pinson and Savéant attempt to discredit the approach and imply that it fails when more than a single rate determining step is involved in a mechanism. It is a simple matter to test this conclusion. Three theoretical working curves are presented in Ref. 2 for such a case where the "reaction order" approach is alleged to fail. The curves are constructed according to relationship (20) where R is the normalized current ratio in DPSC and θ

$$R = \mathrm{f}(kC_A\theta) \qquad (20)$$

is the pulse width. It is clear that this representation fits general relationship (18). What the calculations add is that it is possible to determine the two parameters k_1 and K_1 if the mechanism assignment is correct. *However, working curves are not unique to a particular mechanism.* This particular example is an excellent demonstration of this. The results presented here show that the working curves apply to the mechanism in Scheme 1 as well and that the activation parameters are inconsistent with eqn. (1). Amatore, Pinson and Savéant have made the fundamental mistake of assuming that a data fit to a theoretical working curve is sufficient to establish a mechanism. What this does show is that there are definite limitations to the use of theoretical calculations in mechanism assignment. This is precisely the fact that led to the development of the "reaction order" approach.[19,36,37,39]

We can now examine the implication [2] that the "reaction order" approach was known in 1963.[38] The paper cited deals with the peak potential shift in linear sweep voltammetry brought about by reactions (21) and (22).

$$\mathrm{O} \overset{(ne)}{\rightleftharpoons} \mathrm{R} \qquad (21)$$

$$\mathrm{mR} \xrightarrow{k} \mathrm{P} \qquad (22)$$

The effect of the kinetics on the peak potential was summarized by the following sentence. "Le potentiel de pic varie linéairement avec log v et log C, les pentes étant respectivement, à 25 °C, de $60/n(m+1)$ mV/unité de log v et $(m-1)/(m+1) \cdot 60/m$ mV/unité de log C". We agree that the latter represents the use of a *reaction order* but has no bearing whatsoever on the DCV and DPSC methods that we use in kinetic studieds. In the primary paper on this subject [36] reference is made to the discussion by Bezilla and Maloy on reaction orders in electrode measurements.[40] The latter was in conjunction with the use of theoretical working curves. It is difficult to find justification for the implications made by Amatore, Pinson and Savéant.[2,3]

Conclusions. We conclude that the question raised by Amatore, Pinson and Savéant [2] relating to whether or not a simple dimerization of anion radicals ever takes place has not been answered. Our data clearly show that it does not take place during the dimerization of 9-substituted anthracene anion radicals as they emphatically concluded. In this paper we have addressed the question as to whether or not low or negative activation enthalpies are consistent with the one step mechanism. Our conclusion is that they are *not* and that such evidence is of great value in treating reactions for which kinetic data are consistent with either one step or complex reaction schemes.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures were those described earlier.[41] Reagent grade DMF and DMSO containing the supporting electrolyte (Bu_4NBF_4) were passed through a column containing neutral alumina before use. 9-Nitroanthracene (Fluka, *purum*) and 9-cyanoanthracene (EGA-Chemie) were recrystallized from 1-propanol prior to use. DPSC was carried out by potential steps from about 300 mV less negative than E_{rev} to about 300 mV more negative at 50 s intervals between measurements. Derivative cyclic voltammetry experiments were carried out as previously described.[42]

NOTE

After the writing of this paper was completed another note appeared by Amatore, Pinson and Savéant dealing with the effect of water on the dimerization of $AN-CN^{-}$ in DMSO.[43] At very high water concentrations (up to 16 M) they found that the apparent rate was greater than can be accounted for by our eqn. (5) and they suggest some contribution of the dimerization of $AN-CN^{-}/H_2O$. Although this is a natural consequence of going to high enough $[H_2O]$ so that equilibrium (6) provides high enough concentrations of the complex, we do not agree that their data prove this effect. The bulk properties of aprotic solvents like DMSO do not change appreciably by addition of water up to about 5 % but do change significantly at higher proportions of water.[44–46] It was for this reason that we limited our water concentration to about 5 %. The transition state for the formation of the dimer dianion, regardless of the exact mechanism, is highly polar since there is a localization of charge in the two monomer entities. Therefore, going to a more polar solvent system is likely to cause an increase in rate. Thus, it is surely not safe to conclude that a mechanism change takes place in going to the very high water concentrations. The effect can just as well be explained by the change in the bulk properties of the solvent. In any event, the authors [43] neglect to consider this possibility and therefore their mechanistic conclusions must be viewed with suspicion. These suspicions have been confirmed by a reinvestigation of the linear sweep voltammetry and DCV behaviour of AN−CN in both DMF and DMSO with water concentrations as high as 16 M.[47]

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