

The Kinetics and Mechanism of Diazoalkane Anion Radical Reactions. The Dimerization of Diazofluorene Anion Radical

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Kinetic studies were carried out on the dimer forming reactions of 9-diazofluorene ($\text{Fl}=\text{N}_2$) anion radical generated at electrodes in both acetonitrile and *N,N*-dimethylformamide (DMF). The principal difference found between the behaviour in the two different solvents is that the heterogeneous rate constant is significantly greater in acetonitrile. This fact explains why the oxidation of the anion radical can be resolved from oxidation processes involving further reaction products in acetonitrile but not in DMF allowing direct kinetic measurements to be made in the former case. The reaction was observed to conform to rate law (i) which is consistent with either simple irreversible dimerization or reversible dimerization followed by unimolecular decomposition of the initially formed dimer. The simple

$$\text{Rate} = k_{\text{app}} [\text{Fl}=\text{N}_2^-] \quad (\text{i})$$

irreversible dimerization mechanism was ruled out by a temperature study; the apparent activation energy was found to be only 2.2 kcal/mol. The apparent rate constant was dependent upon the tetraalkylammonium cation of the electrolyte, decreasing progressively as the cation became larger. The apparent heterogeneous rate constant was observed to be greatest when Et_4N^+ was the counter ion, and to decrease progressively in the order $\text{Pr}_4\text{N}^+ > \text{Me}_4\text{N}^+ > \text{Bu}_4\text{N}^+$. The cation effect on the apparent rate constant for dimerization was explained by assuming that the degree of ion pair formation is inversely related to the cation size and that ion association enhances the rate of dimerization by decreasing the charge repulsion between the anion radicals in the transition state.

Diazoalkane anion radicals have recently been proposed to be sources of carbene anion radicals

in solution.^{2–5} On the basis of a cyclic voltammetric investigation² it was proposed that the initially formed diazoalkane radical anion rapidly loses nitrogen in a unimolecular process giving the related carbene anion radical, which then either attacks a molecule of diazoalkane or abstracts a hydrogen atom from the medium. A further proposal is that the carbene anion radical from diazofluorene ($\text{Fl}=\text{N}_2$) is sufficiently stable to be observed as a part of a reversible redox couple during cyclic voltammetry at low sweep rates (75 mV s^{-1}). The latter proposal was shown to be unlikely when it was found that the redox couple assigned to the oxidation and reduction of fluorenylidene anion radical and the parent species is actually a part of a two consecutive one electron redox system, which if the original interpretation³ were correct would require that fluorenylidene dianion be stable in solution as well.⁶ Kinetic studies were carried out by linear sweep voltammetry (LSV) on the reaction in acetonitrile and the results indicated that the kinetics are consistent with rate law (1) which suggested that a simple

$$\text{Rate} = k_{\text{app}} [\text{Fl}=\text{N}_2^-] \quad (1)$$

irreversible dimerization of $\text{Fl}=\text{N}_2^-$ (2) was the probable reaction pathway. This work was reported



as a preliminary communication of the present investigation.¹

The mechanisms of ion radical dimer forming reactions have recently been drawn into focus by

the reports that ion radical–substrate coupling takes place preferentially to ion radical dimerization in a number of cases. The first conclusive evidence for the latter mechanism was found for the reactions of 4,4'-dimethoxystilbene cation radical in acetonitrile.⁷ This reaction had previously been investigated by cyclic voltammetry,⁸ spectroelectrochemistry⁹ and rotating ring disk electrode voltammetry.¹⁰ The kinetic investigations resulted in the proposal that the primary step in the dimer forming reaction is the coupling of cation radicals.^{9,10} For many years electrohydrodimerization (EHD) of activated olefins has been considered to go by the anion radical dimerization mechanism.^{11–14} However, when proton donors are effectively removed from the reaction media, kinetic data show that the anion radical–substrate coupling mechanism predominates.^{15,16} Furthermore, the EHD reaction in the presence of proton donors follows kinetics which are inconsistent with the simple dimerization.¹⁷

Our observation of rate law (1) for the reaction of $\text{Fl}=\text{N}_2^-$ in acetonitrile suggested that this system might serve as a model for anion radical dimerization reactions. As yet, no reliable activation parameters are available and a simple anion radical dimerization mechanism has not been demonstrated rigorously in any case. In this paper we report the details of our kinetic investigation of the second order reaction of $\text{Fl}=\text{N}_2^-$ in acetonitrile.

RESULTS

Cyclic voltammetric studies of the reduction of $\text{Fl}=\text{N}_2$ in acetonitrile and DMF. In our preliminary report¹ we pointed out that attempts to carry out LSV kinetic studies during the reduction of $\text{Fl}=\text{N}_2$ in DMF were unsuccessful. This was due both to the irreproducibility in the response and to the apparent interference of heterogeneous charge transfer kinetics. We have now carried out a qualitative cyclic voltammetric study of the reduction of $\text{Fl}=\text{N}_2$ in acetonitrile and DMF under identical conditions with Me_4NBF_4 as supporting electrolyte. The voltammograms measured in acetonitrile at 50, 5 and 0.5 V s^{-1} are illustrated in Fig. 1. At the highest sweep rate, a high recovery of substrate by oxidation of the anion radical is observed at O_1 . In addition O_2 , about 200 mV more positive than O_1 , is observed, due to the oxidation of an intermediate of further reaction.

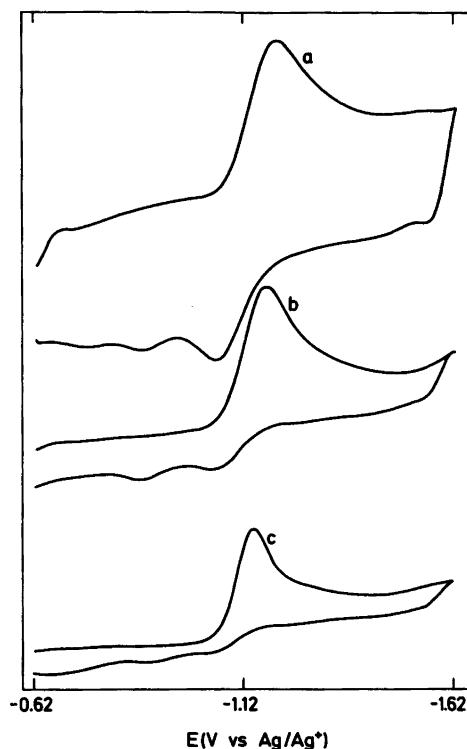


Fig. 1. Cyclic voltammograms for the reduction of $\text{Fl}=\text{N}_2$ in acetonitrile containing Me_4NBF_4 (sat.) at 50 (a), 5 (b) and 0.5 V s^{-1} (c). Upper and lower potential limits, -0.62 and -1.62 V vs. Ag/Ag^+ , respectively.

Decreasing the sweep rate to 5 V s^{-1} was accompanied by a decrease in the peak height for oxidation of $\text{Fl}=\text{N}_2^-$ but not an increase in the height of O_2 . This means that O_2 is not due to a stable reaction product. At 0.5 V s^{-1} , both O_1 and O_2 are greatly diminished in height. When the solvent was DMF, the peak for the oxidation of $\text{Fl}=\text{N}_2^-$ (O_1) was broadened by a shoulder due to O_2 . At 5 V s^{-1} , O_1 and O_2 are evident but overlapped. At 0.5 V s^{-1} only O_2 is seen on the reverse scan. Two conclusions can be drawn from the voltammograms; (i) The reactions following charge transfer are similar in the two solvents and (ii) charge transfer to $\text{Fl}=\text{N}_2$ is slower in DMF which brings about the merging of the peaks for oxidation of $\text{Fl}=\text{N}_2^-$ (O_1) and the oxidation of the intermediate (O_2). The first conclusion is strongly supported by the fact that fluorenone azine ($\text{Fl}=\text{N}-\text{N}=\text{Fl}$) and the corre-

sponding anions are the species which can be identified by cyclic voltammetry at low sweep rates in both solvents.^{1,3,6} The overlapping of oxidation peaks leading to the second conclusion precludes the use of direct kinetic methods to study the mechanism in DMF.

Supporting electrolyte cation effects on heterogeneous charge transfer. Slow heterogeneous charge transfer has a distorting effect on cyclic voltammograms.¹⁸ The rate of charge transfer during the reduction of a number of organic molecules has been observed to be significantly increased in going from large to small tetraalkylammonium ions as the supporting electrolyte counter ion.^{19,20} The effect of the nature of the supporting electrolyte cation on the reduction of $\text{Fl}=\text{N}_2$ is demonstrated by the data in Table 1. Cyclic voltammetric peak potential separations were determined by derivative measurements²¹ at four different voltage sweep rates for solutions of $\text{Fl}=\text{N}_2$ (1.0 mM) in acetonitrile containing either Bu_4N^+ , Pr_4N^+ , Et_4N^+ or Me_4N^+ . Since charge transfer is followed by a rapid chemical

Table 1. The effect of the supporting electrolyte cation on the rate of heterogeneous charge transfer to $\text{Fl}=\text{N}_2$ in acetonitrile.^a

$v/\text{V s}^{-1}$	$\Delta E^p/\text{mV}$	$(k_s)_{\text{app}}^b/\text{cms}^{-1}$
Bu_4N^+		
10	91.7(0.3)	
20	108.8(0.2)	
50	145.4(0.4)	
100	180.8(0.3)	0.066
Pr_4N^+		
10	69.4(0.4)	
20	69.3(0.1)	
50	75.3(0.2)	
100	84.7(0.3)	0.31
Et_4N^+		
10	64.6(0.2)	
20	63.3(0.4)	
50	65.0(0.4)	
100	69.1(0.2)	0.76
Me_4N^+		
10	71.4(0.2)	
20	71.4(0.4)	
50	78.6(0.3)	
100	88.3(0.5)	0.27

^aThe counter ion was BF_4^- in all cases and the supporting electrolyte concentration was 0.1 M except for Me_4NBF_4 (sat.). Measurements at 13.0 °C by derivative cyclic voltammetry according to Ref. 21. ^bCalculated from the peak separation at 100 V s^{-1} assuming the diffusion coefficient of $\text{Fl}=\text{N}_2$ to be $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

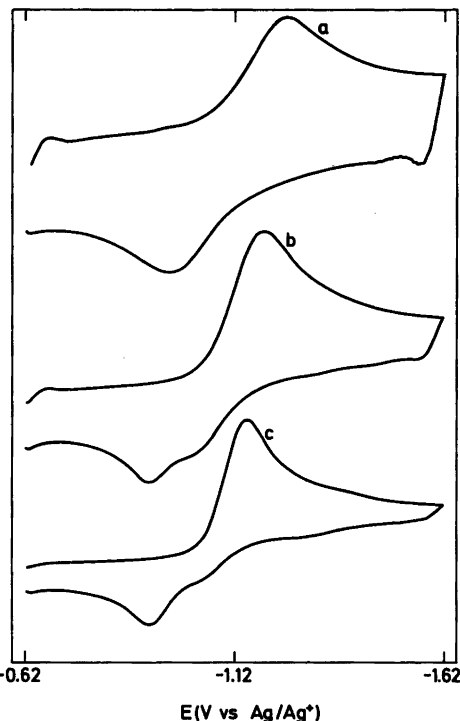


Fig. 2. Cyclic voltammograms for the reduction of $\text{Fl}=\text{N}_2$ in DMF containing Me_4NBF_4 (0.1 M) at 50 (a), 5 (b) and 0.5 V s^{-1} (c). Upper and lower potential limits, -0.62 and -1.62 V vs. Ag/Ag^+ , respectively.

reaction, the data obtained at the highest sweep rate are the most reliable to use in estimating the heterogeneous charge transfer rate constants. The values estimated using the theoretical data derived by Nicholson¹⁸ are listed in the last column of Table 1. Two noteworthy features of the data are (i) the apparent heterogeneous rate constant $(k_s)_{\text{app}}$ is significantly lower with Bu_4N^+ as the counter ion than with any of the other tetraalkylammonium ions and (ii) the value for Me_4N^+ appears to be somewhat lower than would be expected from the trend observed with the other cations.

The sluggish charge transfer in the presence of Bu_4N^+ is further demonstrated by the cyclic voltammograms shown in Fig. 3. In the presence of Pr_4N^+ (a), the voltammogram has the expected appearance for a well-behaved quasi-reversible system while in the presence of Bu_4N^+ (b) the reduction reaction is accompanied by a distorted voltammetric peak.

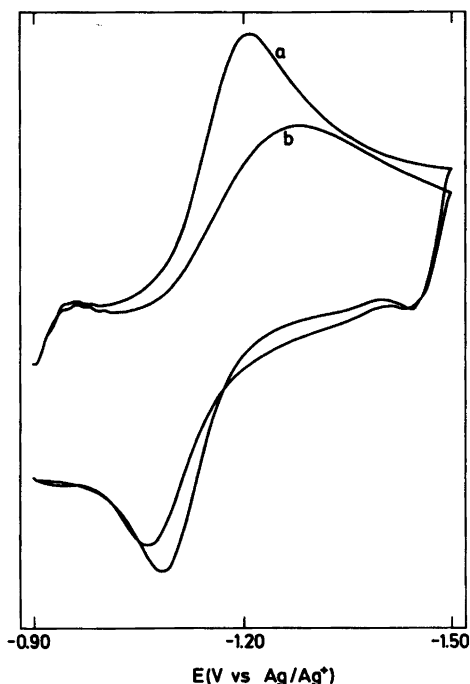


Fig. 3. Cyclic voltammograms for the reduction of $\text{FI}=\text{N}_2$ in acetonitrile containing Pr_4NBF_4 (a) and Bu_4NBF_4 (b) at 100 V s^{-1} . Upper and lower potential limits, -0.90 and $-1.50 \text{ V vs. Ag/Ag}^+$. Supporting electrolyte concentration was 0.10 M . Substrate concentration 1.0 mM .

Since the homogeneous reactions following charge transfer are relatively rapid during the reduction of $\text{FI}=\text{N}_2$, no attempts were made to refine the heterogeneous charge transfer kinetic measurements.

Homogeneous kinetic methods. The methods used are the newly developed ones which do not require first assuming a mechanism and then fitting experimental to theoretical data based upon the proposed mechanism as is conventionally done. The methods are based on eqn. (3) which states

$$\text{Observable} = f(kC_A^z/V) \quad (3)$$

that the transient observable is a function of the apparent rate constant, the substrate concentration (C_A^z) to the appropriate power and the experimental variable V .^{21,22} When the transient technique is derivative cyclic voltammetry (DCV) or double potential step chronoamperometry (DPSC), the

observables are R'_1 and R_1 defined as the ratio of the derivative peak heights on the reverse and forward scans of a cyclic voltammogram or the normalized (by dividing by $1-2^{-z}$) current ratio measured at 2τ and τ where the latter is the pulse width. The variables V are the voltage sweep rate (v) and $(1/\tau)$. A value of the observable which is conveniently measured is chosen and held constant by making the appropriate changes in V while some other parameter of interest; substrate concentration, temperature, isotopic content of the reactants, etc., is changed. When R'_1 and R_1 are held constant at 0.500 , the corresponding variables are $v_{1/2}$ and $(1/\tau)_{1/2}$ and the rate constants can be evaluated from these when the mechanism is one of the standard ones.^{21,23}

The reaction order, $R_{A/B}$, which takes into account participation of both B (which is always the case) and A in the reactions following charge transfer (4) is an important mechanistic quantity and is



defined²¹ by (5) and can conveniently be evaluated by the value of z necessary for (6) to hold.

$$R_{A/B} = 1 + z \quad (5)$$

$$V_{1/2} C_A^{-z} = \text{constant} \quad (6)$$

Reaction order analysis during reduction of $\text{FI}=\text{N}_2$. Analyses were carried out using both DCV and DPSC on the reactions of $\text{FI}=\text{N}_2^-$ generated in acetonitrile. DPSC was used for analysis of the reaction carried out in the presence of Me_4N^+ and the data are summarized in Table 2. The concentration of $\text{FI}=\text{N}_2$ was varied from 0.25 up to 2.0 mM and the third column shows that (6) holds with $z=1$. This result can then be used to obtain the reaction order $R_{A/B}=2$. Results reported in our preliminary communication indicated that both $d(E^p)/d(\log v)$ and $d(E^p)/d(\log C_A)$ for the reaction when the supporting electrolyte cation was Bu_4N^+ in acetonitrile were very close to 19.7 mV/decade at 298 K . Linear sweep voltammetry (LSV) slopes have more recently been directly related to reaction orders by linear equations.²⁴ In the present case, the abbreviated eqns. (7) and (8) where a and b are the reaction orders, R_A and R_B , respectively, indicate that $R_A=0$ and $R_B=2$. Thus,

$$d E^p/d \log v = 1/(b+1) \ln 10 RT/nF \quad (7)$$

Table 2. Effect of substrate concentration on the rate of dimerization of $\text{Fl}=\text{N}_2^-$ in acetonitrile.^a

$[\text{Fl}=\text{N}_2^-]/\text{mM}$	$(\tau_{1/2}/\text{ms})^b$	$(1/\tau_{1/2}C_A)/\text{M}^{-1}\text{s}^{-1}$	$(10^{-5})k/\text{M}^{-1}\text{s}^{-1}$
0.25	13.93	287	2.47
0.50	7.51	266	2.29
1.00	3.61	277	2.38
2.00	2.07	242	2.08
			2.31 (0.17)

^aIn the presence of Me_4NBF_4 (sat.) at 23 °C. ^bPulse width during double potential step experiments necessary for the normalized current ratio, R_B , to equal 0.500.

Table 3. Derivative cyclic voltammetric kinetics of the dimerization of $\text{Fl}=\text{N}_2^-$ in acetonitrile in the presence of Et_4N^+ ion.^a

$[\text{Fl}=\text{N}_2^-]/\text{mM}$	$(v_{1/2}/\text{V s}^{-1})^b$	$(v_{1/2}/C_A)/\text{V M}^{-1}\text{s}^{-1}$	$(10^{-5})k/\text{M}^{-1}\text{s}^{-1}$
0.40	10.8	27.0	1.22
0.80	22.5	28.1	1.27
1.60	46.5	29.1	1.31
3.20	91.0	28.4	1.28
			1.27 (0.03)

^aIn solvent containing Et_4NBF_4 (0.1 M) at 13 °C. ^bThe voltage sweep rate necessary for the derivative current ratio R'_i to equal 0.500.

$$dE^p/d \log C_A = (a+b-1)/(b+1) \ln 10 RT/nF \quad (8)$$

a value of 2 for $R_{A/B}$ is consistent with the LSV study.¹

Data obtained by DCV in the presence of Et_4NBF_4 are summarized in Table 3. Here again, $v_{1/2}/C_A$ is constant indicating that $R_{A/B}$ is 2. As before, in order to be consistent with the LSV study, reaction orders $R_A=0$ and $R_B=2$ must be assigned.

The last columns in Tables 2 and 3 give the apparent rate constants, assuming rate law (1). The mean values are $2.31 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ when Me_4N^+ was the supporting electrolyte cation at 23 °C and $1.27 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ when Et_4NBF_4 was the supporting electrolyte at 13 °C.

Cation effects on the homogeneous reaction rate. In order to have a direct comparison of the apparent rate constants under conditions where only the supporting electrolyte cation was varied, DPSC studies were carried out at ~ 11 °C. The apparent rate constant was observed to increase progressively as the tetraalkylammonium ion became smaller over an order of magnitude range of k_{app} . The data are summarized in Table 4.

Table 4. The effect of the nature of the supporting electrolyte cation on the rate of dimerization of $\text{Fl}=\text{N}_2^-$ in acetonitrile.^a

$R_4\text{N}^+$	$t/^\circ\text{C}$	$\tau_{1/2}/\text{ms}$	$(10^{-5})k/\text{M}^{-1}\text{s}^{-1}$
Bu_4N^+	10.6	40.3	0.214
Pr_4N^+	11.1	7.04	1.22
Et_4N^+	11.5	5.53	1.56
Me_4N^+	11.1	4.02	2.14

^aThe counter ion was in all cases BF_4^- and the supporting electrolyte concentration was 0.1 M in all cases but Me_4NBF_4 (sat.).

The effect of temperature on the rate of reaction of $\text{Fl}=\text{N}_2^-$. Apparent second order rate constants for the reaction of $\text{Fl}=\text{N}_2^-$ in acetonitrile containing Me_4NBF_4 (sat.) were obtained over a 40 degree temperature interval. As shown in Table 5, the apparent rate constant was only slightly affected by the temperature. Linear regression analysis of the data resulted in $E_a=2.2 \text{ kcal/mol}$ with a correlation coefficient of 0.976.

Table 5. The effect of temperature on the rate of dimerization of $\text{Fl}=\text{N}_2^-$ in acetonitrile.^a

$t/^\circ\text{C}$	τ_4/ms	$(10^{-5})k/\text{M}^{-1}\text{s}^{-1}$
-0.2	4.79	1.80
11.1	4.02	2.15
21.0	3.32	2.59
31.0	2.97	2.90
41.1	2.91	2.96

^aIn solvent containing Me_4BF_4 (sat.) with substrate concentration equal to 1.0 mM.

DISCUSSION

The data presented in this study along with the previous LSV work¹ and the low temperature cyclic voltammetry⁶ on the reactions of $\text{Fl}=\text{N}_2^-$ in DMF and acetonitrile so clearly rule out the proposal by MacDonald and Hawley and co-workers of unimolecular decomposition to the carbene anion radical (eqn. 9)²⁻⁵, that little appears to be gained by prolonging that discussion. However, it should be pointed out that the data on which the erroneous conclusions were based were obtained under unfortunate choices of reaction conditions. The work was carried out at room temperature in DMF. If the temperature had been varied especially to lower values it would have been discovered that the redox couple proposed³ to involve fluorenylidene anion radical (Fl^-) was



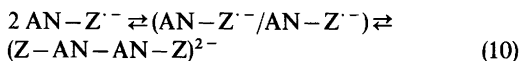
actually associated with another reversible redox couple⁶ which would require that Fl^{2-} be stable as well. Only Bu_4N^+ was used as the supporting electrolyte cation. Use of tetraalkylammonium ions smaller than Bu_4N^+ during cyclic voltammetry at high sweep rates would have shown that the reactions following the quasi-reversible charge transfer can be "out-run" and that direct kinetic methods could be applied. Most of the conclusions were based on reactions conducted in DMF. Our results indicate that not only is the electrochemical response more reliable (in this case) in acetonitrile than in DMF but the charge transfer rate is also enhanced making direct kinetic studies possible.

Our kinetic data only pertain to the initial reactions of $\text{Fl}=\text{N}_2^-$. It is obvious from the low temperature cyclic voltammetry study⁶ that several

intermediates are formed before the final products, $\text{Fl}-\text{N}=\text{N}-\text{Fl}$ and the corresponding anions. Thus, our discussion will necessarily be incomplete, a situation usually encountered in the discussion of the mechanisms of complex reactions. However, we will attempt to construct the mechanism in detail and to indicate what aspects remain speculative. Two intermediates of the reaction remain unidentified and we will refer to them as I-1 and I-2. The first, I-1, was observed only at low temperatures during CV of $\text{Fl}=\text{N}_2$ in DMF⁶ and was shown to be a precursor of the second, I-2. The intermediate previously proposed to be Fl^- by McDonald and Hawley³ is I-2.

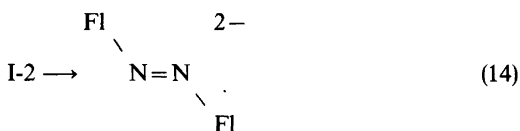
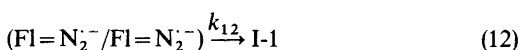
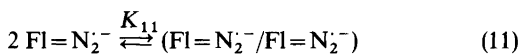
A pertinent point is whether the initial dimerization of $\text{Fl}=\text{N}_2^-$ is reversible or not. We are able to answer this question from the kinetic data. If reaction (2) were irreversible as written, an Arrhenius activation energy characteristic of the dimerization of ion radicals is to be expected. No direct data exist for comparison although Bard, Maloy and coworkers^{11,12} suggest that 4 kcal/mol is a reasonable value for a reaction with a second order rate constant of $10^2 \text{ M}^{-1} \text{ s}^{-1}$. However, that interpretation has been criticized^{16,17} and the data in question shown not to refer to an anion radical dimerization. The dimerization of 4-methoxybiphenyl cation radical has been established as an authentic case of an ion radical coupling reaction.²⁵ Based on that model and our k_{app} for the reactions of $\text{Fl}=\text{N}_2^-$ in acetonitrile of the order of $10^5 \text{ M}^{-1} \text{ s}^{-1}$, E_a is expected to be of the order of 10 kcal/mol providing that irreversible reaction (2) is the rate determining step. Our data are clearly inconsistent with this. An apparent E_a of 2.2 kcal/mol was observed. This value would appear to be too low to account for any single step irreversible reaction. Diffusion controlled reactions generally have E_a values of the order of 3–4 kcal/mol.²⁶ Furthermore, the linearity of the Arrhenius plot is poor. Non-linear and inverse temperature effects on electrode processes have recently been discussed and attributed to complex mechanisms involving equilibria.²⁷ Thus, we conclude that the dimerization of $\text{Fl}=\text{N}_2^-$ is probably reversible and followed by irreversible rate determining reactions.

Related dimerizations have recently been studied.²⁸ It was found that the reversible dimerization of anion radicals of anthracenes substituted in the 9-position with electron attracting substituents ($\text{AN}-\text{Z}^-$) follow a mechanism involving an intermediate (10). The structure of the intermediate is



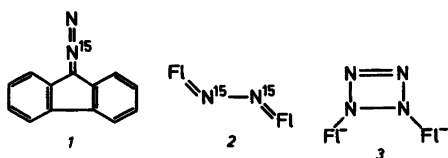
not known but it was proposed to be a complex in which bonding between the two aromatic moieties has not yet taken place. It is conceivable that such an intermediate is also involved in the dimerization of $\text{Fl}=\text{N}_2^{\cdot-}$.

Based on the information at hand, we can suggest a mechanism for the formation of Fl-N=N-Fl^{2-} from $\text{Fl}=\text{N}_2^{\cdot-}$ as outlined below:



The kinetic studies provide the evidence for reactions (11) and (12) while reactions (13) and (14) can be inferred from the low temperature cyclic voltammetric study.⁶

Some elaboration of the evidence presented⁶ for the structures of intermediates I-1 and I-2 is in order. Electrolytic reduction of ^{15}N -labelled substrate (1) resulted in 8% of the product containing two ^{15}N atoms (2). This was suggested to be con-



sistent with the initial generation of dimers at the electrode with possible structure 3 which then initiate the homogeneous chain decomposition of $\text{Fl}=\text{N}_2$, a process which had previously been shown to produce singly labelled product.²⁹ Therefore, it is likely that 2 represents the products formed by the second order dimerization of anion radicals of 1. The subsequent chain reaction which accounts for the predominant amount of product under the conditions of preparative electrolysis

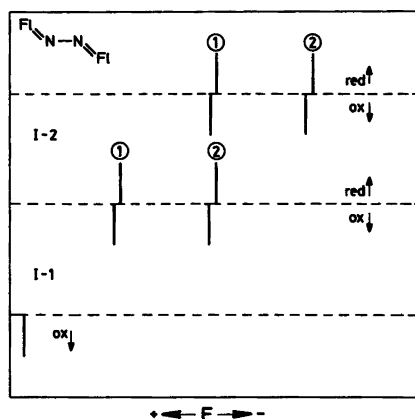
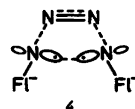


Fig. 4. Schematic diagram of the redox behaviour of the products from dimerization of $\text{Fl}=\text{N}_2^{\cdot-}$.

produces anion radical in concentrations too low to undergo dimerization.

The cyclic voltammetric redox behaviour of the stable reaction product, *s-trans*-fluorenone azine and the intermediates I-1 and I-2 are summarized by the schematic diagram shown in Figure 4. The intermediate observed only at low temperature, I-1, is oxidized in an irreversible process of which I-2 is the product. The potential at which I-1 is oxidized is close to that for fluorene anion⁵ and suggests that the intermediate contains unconjugated Fl^- -groups. Structure 3 was suggested as a candidate for I-1 since the behaviour of 3 would be expected to be consistent with the voltammetry and it has the necessary bonding between labelled nitrogen. However, we have reservations about the intermediacy of 3 since considerable strain must be involved in the formation of the four-membered ring and it is difficult to find electronic arguments which would predict its formation. It is just as likely, perhaps more so due to the strain argument, that 2 is formed from a linear head-to-head dimer via transition state 4. Either structure 3 or transition



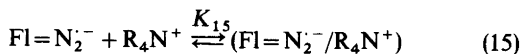
state 4 suggest a likely structure for I-2 to be the dianion of *s-cis*-fluorenone azine.

The question remains as to whether or not the

redox behaviour observed for I-2 is consistent with that species. The pertinent observation is that redox couples 1 and 2 observed for I-2 are of the order of 300 mV less negative than those for *s-trans*-fluorenone azine. The reversible potential of a redox couple gives a measure of the energy difference between the species of differing oxidation states. In this case the potential differences observed indicate that the reduced species of both redox couples 1 and 2 are more stable than the oxidized species by about 300 mV in comparison to the corresponding *s-trans*-fluorenone azine couples. Providing that I-2 is the *s-cis*-fluorenone azine system, the latter requires that the steric interactions present in the *cis*-structures are less severe in the reduced than in the oxidized species. There appears to be only one model system for which data is available for comparison. The reversible reduction potential of *cis*-stilbene in DMF has been reported to be about 60 mV more negative than that for *trans*-stilbene.²⁹ Predictions based on this model would be opposite to that observed for I-2 in comparison with the *trans*-azine. However, we must consider the special situation represented by the fluorenylidene group. In the neutral azine, the Fl= groups are conjugated through overlap of the pi systems with the p orbitals on nitrogen. Total conjugation surely cannot be achieved since it is virtually impossible for the two ring systems to exist in the same plane in the *s-cis*-structure. Uptake of electrons gives rise to the aromatic substituents, Fl⁻, which would be expected to show a decreased need for conjugation to achieve stability. The neutral substituent, Fl⁻ would not be expected to have any unusual stability and would surely require conjugation. This argument then predicts that the reduced species of couples 1 and 2 would be energetically favored relative to those in the *trans*-isomer due to the relief of strain accompanying the lower degree of conjugation. Thus, in our opinion, this qualitative argument can be used to support the previous⁶ assignment of the *s-cis* azine structure to intermediate I-2.

In conclusion we call attention to the apparent discrepancy in the relative rates of heterogeneous charge transfer with the different tetraalkylammonium ions. One might have expected that (k_s)_{app} for the case where the supporting electrolyte cation was Me₄N⁺, should have been the largest. However, we must also consider the effect of ion association on the reversible potential for the reduction of Fl=N₂. The change in the reversible potential,

ΔE_{rev} , brought about by the ion pairing equilibrium (15) is given by (16).³¹ The overall effect is that



$$\Delta E_{rev} = (RT/nF) \ln (1 + K_{15} |R_4N^+|) \quad (16)$$

when K_{15} is significant E_{rev} becomes less negative than the thermodynamic potential, E° . The greater the latter difference, the lower (k_s)_{app} will be if all other factors remain unchanged. Thus, if K_{15} is greater for Me₄N⁺ than for Et₄N⁺, this could account for the apparent discrepancy in the relative rate constants.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures as well as solvent and electrolyte purification were the same as recently described.³² 9-Diazo fluorene was prepared by a standard method.³³

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