Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part 20.[1] Kinetic Studies on Reductively Initiated Electron Transfer Chain Catalysis of the Decomposition of 9-Diazofluorene

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The method of constant-current electrolysis (c.c.e.) at a platinum cathode has been used to investigate the kinetics of the electron transfer chain catalysis of the decomposition of 9-diazofluorene (FlN_2) in CH_3CN solution. Equations have been derived for various possible kinetic forms of both chain propagation and termination, and comparison with observation indicates that the chain carrier reacts with a molecule of FlN_2 to propagate the chain and reacts with the solvent, or other additive such as oxygen or diethyl malonate, to terminate the chain. Interruption of the current in the experiments (i.c.c.e.) leads to a different set of equations from which it is possible to evaluate separately the rate constants for propagation and termination. The identity of the chain carrier is discussed. It is established that this is unlikely to be the diazolalkane anion radical, $FlN_2^{-\bullet}$, as previously thought. Anion-radicals derived from the product fluorenone azine are the likeliest candidates under the reaction conditions used.

It has previously been established both by us[2,3] and by others[4] that addition of an electron to 9-diazofluorene (FlN_2) can initiate a chain decomposition leading to the formation of fluorenone azine (FlN_2Fl) in very high chemical yields. It was suggested initially[4,5] that a key step in the chain was unimolecular loss of molecular nitrogen from the diazolkane anion-radical generating a short-lived carbene anion radical. The use of transient electrochemical techniques, however, strongly suggested that dimerisation of $FlN_2^{-\bullet}$ is the favoured reaction path (with a second-order rate constant of 2×10^5 l mol^{-1} s^{-1} at 23 °C) under the conditions of the voltammetric and double-step chronamperometric experiments.[2,6] Recently, pulse radiolysis experiments on FlN_2 have been interpreted in terms of $FlN_2^{-\bullet}$ being reversibly protonated and the protonated form dimerising; unimolecular loss of N_2 from $FlN_2^{-\bullet}$ was excluded.[7]

In this paper we address ourselves to the question of the mechanism of the chain reaction under conditions of preparative electrolysis with rather low current densities, and with mechanically stirred reaction solutions. In these circumstances the volume of reaction solution close to the cathode in which the concentrations of reactants and intermediates differ substantially from that in the bulk solution will be relatively smaller than in the quiet solutions used for voltammetric and related experiments.[8] Under these circumstances dimerisation of ion radicals should be less probable and might not provide the major reaction pathway for $FlN_2^{-\bullet}$.

We now report an investigation using constant-current electrolysis[9] (c.c.e.) of the chain decomposition of FlN_2 initiated at a platinum cathode, and use the methods of homogeneous chemical kinetics to analyse the resultant concentration–time curves. In this way we are able to show that propagation of the chains probably involves very rapid reaction of $FlN_2^{-\bullet}$ (with a further molecule of FlN_2 or by dimerisation) to give rise to an intermediate of rather low reduction potential which reacts with a second molecule of FlN_2 in the rate-limiting step. The nature of the chain termination steps which compete with propagation are discussed in the light of observations of the effect of air, oxygen, and other additives on the electrolysis.

Results

All reactions were carried out in CH_3CN–Me_4NBF_4 (sat.) at 30 °C and except where otherwise specified, in an inert atmosphere usually of nitrogen freed of traces of oxygen by passage through Fieser's solution. The glass reactor, usually containing 50 cm^3 of solution, was equipped with a cylindrical smooth platinum cathode separated from the small (volume *ca.* 2 cm^3), centrally located anode compartment by a sintered glass disc. The current, supplied from a conventional constant-current generator, was usually in the range 5—20 mA (density 0.2—0.8 mA cm^{-2}). The cathode compartment was vigorously stirred magnetically throughout the course of the reactions. If this was not done, a deep purple-red colouration could be seen to develop at the cathode, the intensity of the colour varying with the electrolysis conditions. Samples small in relation to the total volume of solution were withdrawn from time to time and the concentration of diazoalkane determined by i.r. spectrophotometry. Figure 1(a) shows a typical concentration–time

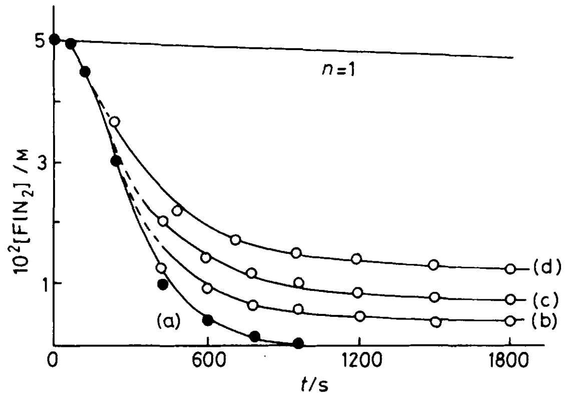

Figure 1. Concentration–time curves for the disappearance of FlN_2: (a) constant-current electrolysis (48 cm^3 of solution in the cathode compartment, 5 mA); current interrupted after 240 s (b), 180 s (c), 120 s (d). Continuous lines are calculated according to equation (11) using the parameters in the text

Table 1. Product analyses from c.c.e. and i.c.c.e. at 30 °C[a]

	C.c.e. N_2	C.c.e. Air	I.c.c.e.[b] N_2	I.c.c.e.[b] Air
FlN_2	0.21	19.7	7.0	49.9
FlN_2Fl	98.8	57.0	92.5	49.0
$Fl{:}NNH_2$	0.39	1.7	N.d.	N.d.
Fl:O	0.30	8.6	0.29	0.18
FlHOH	N.d.	12.0	0.25	0.84
FlH_2	0.27	N.d.	N.d.	N.d.

[a] % FlN_2 (initially 0.05M) converted into each product; n.d. = not detected. [b] Interruption after 240 s at 5 mA; analysis after termination of reaction.

curve with its characteristic sigmoid shape, together with that expected on the basis that one faraday per mol is consumed in the decomposition. A typical product analysis by h.p.l.c. is in Table 1 and shows that under nitrogen there is almost complete conversion of FlN_2 into FlN_2Fl. Indeed, using an initial concentration of FlN_2 of 0.05M, azine is precipitated at an early stage of reaction. Control experiments established, however, that the presence of the azine had no influence on the behaviour of the system either qualitatively or quantitatively.

The shape of curve (a) in Figure 1 is readily interpretable in a qualitative way in terms of (i) a constant rate of initiation determined by the applied current, with a consequent linear increase with time of the concentration of chain carriers; (ii) propagation by reaction of the chain carriers most probably with a molecule of diazoalkane; (iii) termination reactions which become dominant as the residual FlN_2 concentration approaches zero. Confirmation of the chain nature of the reaction comes from the observation that the diazoalkane continues to be consumed after the current is switched off (interrupted constant-current electrolysis, i.c.c.e.), the extent of this further reaction depending on the amount of charge already introduced at the time of interruption of the current [Figure 1, curves (b)—(d)]. Qualitatively similar behaviour was observed over a ten-fold range of initiation rates and a five-fold range of initial reactant concentrations.

The presence of oxygen in the system has a marked effect on the behaviour. If, in electrolyses conducted as before, the current is interrupted and at the same time the reaction solution is saturated with air or oxygen, the disappearance of FlN_2 quickly stops [Figure 2; curves (c), (d)]. The analysis of the products of such reactions, however, shows that only small amounts of FlN_2 have been converted into products other than FlN_2Fl. When the electrolysis is conducted throughout under aerobic conditions, the concentration time–curve takes on a quite different shape [Figure 2; curve (b)] and fluorenone becomes a substantial component of the product mixture (Table 1). Use of unpurified nitrogen (O_2 content *ca.* 100 p.p.m.) gives a sigmoid concentration–time curve, but with a prolonged slow stage initially. All these observations point to oxygen acting as a good terminating reagent in these chain reactions.

Similar i.c.c.e. experiments have been conducted, but with addition of small concentrations of diethyl malonate (DEM), a good proton donor [pK_a 13.3 (H_2O),[10a] 15.7 (DMSO);[10b] *cf.* CH_3CN, pK_a *ca.* 25 (H_2O), 31.3 (DMSO)] or tetrahydronaphthalene (tetralin) which is a much weaker acid, but a good hydrogen-atom donor [relative reactivity towards phenyl radicals, tetralin:$CH_2(CO_2Me)_2$:CH_3CN = 444:18:9].[11] With DEM rapid termination of the reaction occurred upon interruption of the current whereas addition of tetralin at the time of interruption caused little additional termination beyond that observed with no additive.

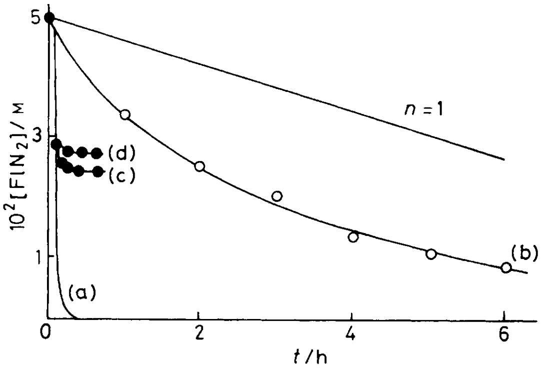

Figure 2. Influence of air and oxygen on c.c.e. and i.c.c.e. experiments. (a) C.c.e. under nitrogen; (b) c.c.e. with continuous air saturation; (c) i.c.c.e. with air saturation at time of interruption; (d) i.c.c.e. with oxygen saturation at interruption.

Kinetic Treatment.—In the light of the qualitative interpretation given above, we attempt here to derive mathematical relations to enable us to simulate the concentration–time curves obtained from constant-current electrolyses. We treat the electrolysis as if it were a system of chemical reactions taking place in homogeneous solution, that is to say, an environment free of concentration gradients; hence the system is assumed to be amenable to treatment by chemical kinetic equations appropriate to homogeneous solution. Such an approach has been quite extensively used previously,[12] but it should be recognised that it does not take explicit account of processes rapid enough to be essentially complete within the region close to the electrode where concentrations differ appreciably from those in the bulk solution. The time scale of such processes will in general be much shorter than that on which the observations described in the previous section were made.

The chain process is outlined in equations (1)—(3), in which the arrows may refer to one or to several reaction steps, C is the chain carrier involved in the rate-limiting step of chain propagation, and X is any species capable of terminating the chain.

$$\text{Initiation: } n\text{FlN}_2 + e^- \longrightarrow \text{C} \qquad (1)$$

$$\text{Propagation: C} + 2\text{FlN}_2 \longrightarrow \text{FlN}_2\text{Fl} + \text{C} \qquad (2)$$

$$\text{Termination: C} + \text{X} \longrightarrow \text{Products} \qquad (3)$$

Assuming that initiation is a one-electron process and is 100% efficient, the rate of initiation (in mol l^{-1} s^{-1}) is given by (4) where i is the constant current and V the volume of solution in the cathode compartment. The termination rate depends on the termination reaction and its kinetic form; X could be a solvent molecule capable of proton or hydrogen-atom donation, an extraneous impurity in the system, or it could be another carrier species C. In general, the time variation of the concentration of C will be given by (5) which on integration yields different expressions for the instantaneous value $[C]_t$ depending on the nature of the termination process.

$$v_i = i/FV \qquad (4)$$

$$d[C]/dt = v_i - k_T[C][X] \qquad (5)$$

In Table 2 are the expressions for first-order termination ([X] is constant; $k'_T = k_T[X]$) and second-order termination. If propagation is taken to be much faster than initiation, then the

Table 2. Influence of termination processes on the chain carrier concentration and FlN_2 disappearance

Termination	$[C]_{t\,(or\ \tau)}$	$\int_0^{t(\tau)} 2k_p[C]_{t(\tau)}dt(\tau) = y$*
$C\ (+X) \xrightarrow{k'_T}$	$\frac{v_I}{k'_T}(1 - e^{-k'_T t})$	$\frac{2k_p v_I}{k'_T}\left[t - \frac{1}{k'_T}(1 - e^{-k'_T t})\right]$
	$[C]_i\, e^{-k'_T \tau}$	$\frac{2k_p}{k'_T}[C]_i\,(1 - e^{-k'_T \tau})$
$2C \xrightarrow{k_T}$	$(v_I/k_T)^{\frac{1}{2}}\tanh\,(v_I k_T)^{\frac{1}{2}}t$	$\frac{2k_p}{k_T}\{\ln[\cosh\,(v_I k_T)^{\frac{1}{2}}t]\}$
	$[C]_i/(k_T[C]_i\,\tau + 1)$	$\frac{2k_p}{k_T}\ln\,(k_T[C]_i\,\tau + 1)$

* $y = \int_0^t -d[FlN_2]/[FlN_2]^m$ for c.c.e. experiments and $\int_i^\tau -d[FlN_2]/[FlN_2]^m$ for i.c.c.e. experiments.

rate of product formation and of disappearance of substrate FlN_2 are determined by (2) and given by (6), in which m represents the kinetic order in FlN_2 of the rate-determining step of propagation. The most probable values of m are 0, 1, or 2. Separating the variables in (6) gives (7) and the integrated

$$\frac{d[FlN_2Fl]}{dt} = -\frac{1}{2}\frac{d[FlN_2]}{dt} = k_p[C][FlN_2]^m \qquad (6)$$

$$\int_0^t \frac{-d[FlN_2]}{[FlN_2]^m} = \int_0^t 2k_p[C]dt \qquad (7)$$

forms of the right-hand side for first- and second-order termination are in Table 2.

These equations represent idealised behaviour. In practice the concentration–time curves may deviate from prediction, especially in the late stages of electrolysis when there could be, for example, deterioration of the electrode surface or interference from reaction products. We have, therefore, extended our approach by carrying out experiments in which the current is interrupted (i.c.c.e.); the subsequent homogeneous chemical reactions can, without assumptions, then be treated in a conventional kinetic way, and, provided that rate coefficients for propagation and termination have appropriate magnitudes, values for both can be derived.

For i.c.c.e. experiments we define a modified time variable $\tau = t - t_i$ where t_i is the time at which the current is interrupted. The value of $[C]_\tau$ is then given by $[C]_i f(\tau)$ in which the function $f(\tau)$ depends on the termination process; Table 2 contains expressions for first- and second-order termination. The carrier concentration at the time of interruption $[C]_i$ can be approximated by $v_I t_i$, but can be corrected using the equations for $[C]_t$ once k_T (or k'_T) is known.

For the case of first-order termination and with $m = 1$ in the propagation step the dependence of $[FlN_2]$ on τ is given by (8). Thus, as τ becomes large, the reaction stops and the final diazoalkane concentration is then given by (9), permitting evaluation of $2k_p/k'_T$. Combination of (9) and (8) yields (10)

$$\ln\frac{[FlN_2]_i}{[FlN_2]_\tau} = \frac{2k_p}{k'_T}[C]_i\,(1 - e^{-k'_T\tau}) \qquad (8)$$

$$\ln\frac{[FlN_2]_i}{[FlN_2]_\infty} = \frac{2k_p}{k'_T}[C]_i \qquad (9)$$

Table 3. I.c.c.e. experiments

$10^4 v_I t_i$	Additive[a]	$\ln\frac{[FlN_2]_i}{[FlN_2]_\infty}$	$10^4[C]_i$/M[b]	$10^{-4}(2k_p/k'_T)$
1.30		1.32	1.17	1.13
1.94		1.73	1.67	1.04
1.94[c]		3.85[c]	1.92[c]	2.01[c]
2.59		2.35	2.13	1.10
2.59	Air (sat.)	0.155	2.13	0.073
2.59	O_2 (sat.)	0.033	2.13	0.0155
2.59	DEM (5 mM)	0.169	2.13	0.079
2.59	Tetralin (5 mM)	1.76	2.13	0.83

[a] Added at t_i. [b] Calculated using $[C]_i = \frac{v_I}{k'_T}(1 - e^{-k'_T t_i})$ using $k'_T = 1.7 \times 10^{-3}\ s^{-1}$ for reactions in CH_3CN. [c] CD_3CN as solvent: application of (10) gave an approximate value of $8 \times 10^{-4}\ s^{-1}$ for k'_T.

from which it can be seen that k'_T is derivable from experimental results; k_p can thus also be separably determined. For second-order termination the equation analogous to (8) (see Table 2) predicts that as $\tau \rightarrow \infty$, $[FlN_2]_\tau \rightarrow 0$.

$$\ln\left[1 - \left\{\frac{\ln([FlN_2]_i/[FlN_2]_\tau)}{\ln([FlN_2]_i/[FlN_2]_\infty)}\right\}\right] = -k'_T\tau \qquad (10)$$

Discussion

The results in Figure 1 are clearly indicative of a termination process which is first order in the chain carrier. Interrupting the current at various stages in the electrolysis leads to incomplete disappearance of FlN_2 as required by (8). The results represented numerically in Table 3 using $[C]_i = v_I t_i$ show the behaviour predicted by (9) with $2k_p/k'_T = 0.94 \times 10^4\ l\ mol^{-1}$. Treatment of the data from the curves in Figure 1 according to (10) yielded linear plots, and linear regression analysis afforded the following values of $10^3\ k'_T/s^{-1}$ for interruption after 120, 180, and 240 s, respectively: 1.69 ± 0.14, 1.73 ± 0.15, and 2.19 ± 0.03. After correction of $[C]_i$ using $k'_T = 1.7 \times 10^{-3}\ s^{-1}$ in the appropriate equation from Table 2, the average value of $2k_p/k'_T$ is $1.09 \times 10^4\ l\ mol^{-1}$ and $k_p = 9.7\ l\ mol^{-1}\ s^{-1}$. With these values, the curves in Figure 1 were calculated using (11). The fit is visually very good over the whole course of the reaction, and similarly good agreement between calculation and experiment was achieved for reactions carried out with widely different initiation rates and initial $[FlN_2]$.

$$\ln\frac{[FlN_2]_0}{[FlN_2]_t} = \frac{2k_p v_I}{k'_T}\left[t - \frac{1}{k'_T}(1 - e^{-k'_T t})\right] \qquad (11)$$

Attempts to fit the results of c.c.e. experiments to the equations derived on the assumption that termination is second order in C or that $m = 0$ or 2 in the propagation step were unsuccessful. Moreover, the results of the i.c.c.e. experiments in Table 3 are inconsistent with m-values other than unity. For $m = 0$, the condition for a unimolecular reaction of the chain carrier as the rate-limiting step in propagation, $[FlN_2]_i - [FlN_2]_\infty$, should be proportional to $[C]_i$; this is clearly not observed. Dimerisation of C as the key step in propagation can likewise be discounted since this would require proportionality between $[FlN_2]_i - [FlN_2]_\infty$ and $[C]_i^2$. We conclude, then, that propagation involves reaction of the carrier C with FlN_2, and termination is a process obeying a first-order or pseudo-first-order kinetic law.

Two important related questions remain: (i) What is the identity of C? (ii) What is the nature of the termination reactions?

The purple-red species formed at the electrode is related to or could be C. The most obvious structure for C might seem to be that of the diazoalkane anion radical $FlN_2^{-\bullet}$. It is unlikely, however, that this could be so. We have previously established by double-potential-step chronoamperometry that $FlN_2^{-\bullet}$ undergoes dimerisation with a rate constant at 23 °C of 2.3×10^5 l mol^{-1} s^{-1}. Thus, under the present conditions (50 cm^3 of solution; current 5 mA) [C] = *ca.* 10^{-4}M after 100 s and would be consumed by dimerisation at a rate of 2×10^{-3} mol l^{-1} s^{-1}. To compete with this, the reaction of $FlN_2^{-\bullet}$ with FlN_2 (concentration *ca.* 3×10^{-2}M) would need a rate constant (k_p) substantially greater than $2 \times 10^{-3}/(1 \times 10^{-4} \times 3 \times 10^{-2}) \sim 0.7 \times 10^3$ l mol^{-1} s^{-1}, and thus more than 70-fold greater than the value observed in the c.c.e. experiments. Reaction of $FlN_2^{-\bullet}$ with FlN_2 remains a possible reaction, since the rate constant required to make it competitive with dimerisation is not unreasonably large, but it cannot be the rate-determining step of propagation. That must occur later and involve, in the role of C, either the dimer of FlN_2^{-P}, the product of reaction of $FlN_2^{-\bullet}$ and FlN_2, or a species derived from either. For example, *s-trans*-$(FlN_2Fl)^{-\bullet}$ which could result from the reaction of $FlN_2^{-\bullet}$ and FlN_2 by loss of N_2 could be a candidate (see below, however). It would require that this anion-radical transfer its electron to a further molecule of FlN_2 with a rate constant of 9.7 l mol^{-1} s^{-1}. Such a value seems too low for a simple irreversible electron transfer, since the azine is reduced to its radical anion at a potential *ca.* 0.3 V less negative than that at which FlN_2 is reduced. Assuming that the exoergonic electron transfer from $FlN_2^{-\bullet}$ to FlN_2Fl takes place at a diffusion-controlled rate the (maximum) predicted value for the reaction *t*-$(FlN_2Fl)^{-\bullet} + FlN_2 \rightarrow FlN_2Fl + FlN_2^{-\bullet}$ is k = *ca.* 10^5 l mol^{-1} s^{-1}. If the rate-limiting stage of propagation is indeed an electron transfer from C to FlN_2,* then on this basis C should have a reduction potential *ca.* 0.54 V less negative than FlN_2. The dimer of $FlN_2^{-\bullet}$, to which a wave on the reoxidation phase of cyclic voltammograms of FlN_2 run at −50 °C in dimethylformamide–Bu_4NBF_4 has previously been assigned,[6a] has a reduction potential approximately 0.9 V less negative than FlN_2. However, a further reversible wave in cyclic voltammograms of FlN_2 run at temperatures between +20 and −20 °C occurs at a potential *ca.* 0.6 V less negative than the wave for FlN_2 and was assigned by us to the anion-radical of *s-cis*-fluorenone azine.[6a] Low-temperature cyclic voltammetry in CH_3CN gives less clearly defined results, but these suggest some compression of the range of peak potentials. It should be added that in a recent paper [13] the waves which we have assigned to the successive oxidation *cis*-azine^{2-}→*cis*-azine$^{-\bullet}$→*s-cis*-azine have been suggested to be better attributed to successive oxidation steps of this dimeric dianion $(FlN_2)_2^{2-}$. While we do not believe that this new assignment can be correct [since in our experiments the waves in question were seen to arise from a species which had as its precursor an intermediate formed from $FlN_2^{-\bullet}$, arguably $(FlN_2)_2^{2-}$], the possibility that azine anion radicals or $(FlN_2)_2^{2-}$ could be the carrier remains.

Further assistance in choosing between the three possibilities for C comes from a consideration of the termination processes. By measuring the extent of reaction after interruption of the current and introduction of additives air, oxygen, diethyl malonate, and tetrahydronaphthalene (i.c.c.e.), it is possible to evaluate $2k_p/k'_T$. On the assumption that the additives do not modify k_p, then k'_T values can be obtained. The results of such determinations are in Table 3 and establish the following points.

(1) In the absence of additives, termination involves reaction of C with the solvent at least in part by hydrogen abstraction, since changing from CH_3CN to CD_3CN leads to an increase in $2k_p/k'_T$ by a factor of *ca.* 2.

(2) From the values of $2k_p/k'_T$ for diethyl malonate and tetrahydronaphthalene in conjunction with k'_T in the absence of additives, it can be shown that diethyl malonate is at least 40 times more effective as a terminator than tetralin, and over 40 000 times more effective than CH_3CN.

(3) Oxygen is also an effective chain-terminating reagent. Values of k'_T are 2.55×10^{-2} s^{-1} in air and 0.120 s^{-1} when the reaction mixture is saturated with oxygen.† Taken in conjunction with k'_T observed under anaerobic conditions, these values define an excellent straight line (*r* 0.9999) when correlated with the partial pressure of oxygen.

All these results point to termination being represented by (13) where the summation is over all proton donors in the

$$k'_T = \sum_i k_T^{HA_i}[HA_i] + k_T^{O_2}[O_2] \qquad (13)$$

reaction medium. Approximate values of $k_T^{HA_i}$/l mol^{-1} s^{-1} are 1×10^{-4} (CH_3CN), <0.11 (tetralin) and 4.5 (diethyl malonate). Taking the solubility of O_2 in CH_3CN as being the same as in acetone, *viz.*, 1.3×10^{-2}M,[14] the value of $k_T^{O_2}$ is *ca.* 10 l mol^{-1} s^{-1}.

The pattern of results suggests that the chain carrier C has properties akin to those observed with carbanions such as fluorenyl anion [15] rather than those that might be expected of a radical species. The differing reactivity of diethyl malonate and tetrahydronaphthalene is, we believe, particularly significant. The results do not, however, allow an unambiguous conclusion to be drawn regarding the identity of the chain carrier; the *cis*- and *trans*-radical-anions of fluorenone azine or the bis-carbanion resulting from dimerisation of $FlN_2^{-\bullet}$ could fit. However, our earlier observation[6a] that fluorenone azine produced by electrolysis of Fl=^{15}N=N contained only 8 ± 4% of doubly labelled material, thought to arise from $(FlN_2)_2^{2-}$, suggests that the principal pathway for azine formation is $FlN_2^{-\bullet} + FlN_2 \rightarrow N_2 + FlN_2Fl^{-\bullet}$. The azine anion-radical in its *trans*-form should probably be eliminated from consideration on the following grounds. When the reaction solution is saturated with azine, which is reversibly reduced at a lower potential than FlN_2, the *trans*-anion-radical should be present in solution at a fairly constant concentration, and thus be available to bring about electrocatalysis of the FlN_2 decomposition. That such electrocatalysis does not occur is shown by our observation that electrolyses of solutions of much lower initial FlN_2 concentration, in which azine precipitates only late in the reaction, can be simulated using (11) with the same values of v_I, k_p, and k'_T as used at high FlN_2 concentrations.

The reaction products (Table 1) provide relatively little of significance for the identification of C. The yield of azine is always high, and the proportion of other products is related directly to the number of faradays passed. Oxygenated products

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* In support of this, Ph_2CN_2, which is reduced at potentials 0.91 V more negative than FlN_2, is scarcely decomposed in solutions in which FlN_2 is electrolysed.

† Continuous aerobic electrolysis (see Figure 2) can be interpreted in terms of (11). When *t* is *ca.* 200 s the exponential term becomes small and (11) reduces to (12) which indicates a linear dependence of

$$\ln\frac{[FlN_2]_0}{[FlN_2]_t} = \frac{2k_p v_I}{k'_T}\left(t - \frac{1}{k'_T}\right) \qquad (12)$$

$\ln[FlN_2]_t$ on *t* with a slope of $2k_p v_I/k'_T$. Such is indeed observed with a slope of 9×10^{-5} s^{-1}. Assuming that the value of $2k_p/k'_T$ obtained in the i.c.c.e. experiments holds, namely 728 l mol^{-1}, v_I would seem to be *ca.* 1.2×10^{-7} l mol^{-1} s^{-1}. This in turn suggests that most of the current supplied is used in reducing oxygen rather than FlN_2.

are the principal by-products, especially in reactions conducted in air or with aerobic quenching. The detection of fluorenol is noteworthy, as is the observation of fluorene. The latter might imply some diversion of $FlN_2^{-\bullet}$ by hydrogen-atom abstraction from the solvent as for $Ph_2CN_2^{-\bullet}$,[16] but it is also known to be formed together with fluorenone hydrazone, a little fluorenone, and fluorenone fluorenylhydrazone (Fl:NNHFlH) in the electrolysis of fluorenenone azine in DMF in the presence of low concentrations of the proton donor diethyl malonate.[17]

In summary, the present work has demonstrated in detail the chain nature of the electrolysis of FlN_2 in CH_3CN solution and permitted a kinetic analysis of the observed concentration–time curves. The identity of the chain carrier is still not known unambiguously, but it has been shown that it reacts with FlN_2 (k_p *ca.* 10 l mol^{-1} s^{-1}) probably by electron transfer, with O_2 ($k_T^{O_2}$ *ca.* 10 l mol^{-1} s^{-1}) in a process that may involve electron transfer, but leads to oxygenated products, and with proton donors including the solvent. Taken in conjunction with the products, the chain carrier is most probably the *cis*-fluorenone azine anion-radical. Work is in hand to attempt to characterise the species responsible for the transient colour formed at the electrode surface in unstirred reaction solutions.

Experimental

Materials.— 9-Diazofluorene was prepared by oxidation of fluorenone hydrazone[18] and recrystallised from light petroleum, m.p. 91 °C. The only impurity detected by h.p.l.c. analysis was fluorenone (0.019%). Tetramethylammonium tetrafluoroborate (Fluka) and actonitrile (Fluka, puriss, p.a.) were used as supplied; acetonitrile solutions of the salt were, however, dried immediately before use by passage through a column of activated alumina. 'Oxygen-free' nitrogen was purified by passage through a Fieser's train[19] and all gases were saturated with dry acetonitrile before passage into the reactor. Diethyl malonate and tetrahydronaphthalene were middle fractions of redistilled samples.

Constant-current Electrolysis.—The reaction vessel (capacity 80 cm^3) was constructed of glass and was fitted with a cylindrical smooth platinum cathode (surface area 25 cm^2) and platinum anode in a separate centrally located compartment connected by way of a sintered disc. Acetonitrile solutions (50 cm^3) containing Me_4NBF_4 (0.07M) and 9-diazofluorene (usually 0.05M initially) were stirred magnetically and continuously flushed with purified nitrogen. Current was supplied from a conventional constant-current generator, and was usually in the range 5—15 mA. Samples of the reaction mixture (*ca.* 0.25 cm^3) were withdrawn at timed intervals by syringe through a serum cap on one of the ports of the electrolysis vessel and analysed immediately. Contact of the reaction solution with the air effectively stopped the reaction.

I.r. Analysis.—The absorbance of samples of the quenched reaction mixture at 2 050 cm^{-1} was measured in a CaF_2 cell (path length 0.5 mm) using a Perkin-Elmer 257G grating i.r. spectrometer. Concentrations were determined from a calibration curve, since there was some downward deviation from Beer–Lambert behaviour at the higher concentrations.

Product Analyses.—Reaction mixtures were poured into water and extracted with methylene dichloride. The washed and dried extracts were then analysed by h.p.l.c. (Spectra Physics) using a RP18-2776 reverse-phase column and eluting with 85% aqueous acetonitrile. Triphenylethylene was used as an internal standard and integration of signals (u.v. detection at 254 nm) was by Hewlett-Packard type 3390A reporting integrator.

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