Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part 19.[1] Kinetics and Mechanism of the Reactions of 9-Diazofluorene Cation Radical

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The decomposition of 9-diazofluorene (FlN_2) brought about at a platinum anode or by chemical oxidants, $Cu(BF_4)_2$ or $(p\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$, in CH_3CN solution leads to formation of mixtures of bifluorenylidene and fluorenone azine in high yield. The reactions have been studied kinetically by conventional means and using the transient electrochemical techniques derivative linear sweep voltammetry (l.s.v.) and derivative cyclic voltammetry (d.c.v.). Constant-current electrolysis of FlN_2 shows the characteristics of a chain process. The chemical oxidants give rise to a rate law $-d[FlN_2]/dt = k[FlN_2][oxidant]$ above a critical oxidant level, and the value of k is the same for both oxidants, even though their oxidation potentials are substantially different. It is inferred that the process studied is the chain propagation step in which the chain carrier reacts with a molecule of FlN_2. Under the conditions of l.s.v. and d.c.v. experiments, it is shown that the instantaneously formed $FlN_2^{+\bullet}$ is consumed in a rapid process which is second order with respect to the cation radical and has a rate constant of 1.9×10^8 l mol^{-1} s^{-1}; it is suggested that this process is cation radical dimerisation. Since the product of this step rapidly yields bifluorenylidene, it is argued that the slower macroscopic chain reactions do not involve dimerisation, but rather that $FlN_2^{+\bullet}$ rapidly attacks a further FlN_2 molecule to generate the chain carrier which must have a lower oxidation potential than $FlN_2^{+\bullet}$. Possible structures for the chain carrier are considered in the light of earlier e.s.r. evidence for a radical intermediate.

Much interest has recently been shown in electron-transfer chain (e.t.c.) catalysis of organic reactions[2-4] in which a transformation which overall is neither an oxidation nor a reduction is nevertheless catalysed by substances capable of one-electron oxidation or reduction. Despite this interest there has been relatively little detailed kinetic study of such reactions. A reaction in this category which has attracted attention is the decomposition of aryldiazoalkanes brought about by one-electron oxidation, for example by copper(II) salts with non-nucleophilic anions in aprotic solvents,[5-8] or electrochemically.[9] In the case of diazodiphenylmethane (Ph_2CN_2), the product of such reaction in CH_3CN solution consists largely of tetraphenylethylene together with a little benzophenone azine; less polar solvents lead to a reversal of the relative proportions of these two products.[6] We previously showed that the rate of disappearance of Ph_2CN_2 in CH_3CN obeyed the rate law $-d[Ph_2CN_2]/dt = k_2[Ph_2CN_2][catalyst]$ with $k_2 = 117$ l mol^{-1} s^{-1} at 30 °C independent of whether the catalyst was $Cu(ClO_4)_2$ or $(p\text{-}BrC_6H_4)_3N^{+\bullet}ClO_4^-$. It was inferred at the time that the rate-limiting step in the reaction is the attack of the rapidly formed diazoalkane cation radical, $Ph_2CN_2^{+\bullet}$, on a further molecule of Ph_2CN_2 to give, after loss of molecular nitrogen, either the cation radical of tetraphenylethylene or benzophenone azine. These two, by electron abstraction most probably from Ph_2CN_2, were thought to regenerate $Ph_2CN_2^{+\bullet}$, thereby completing the chain. E.s.r. spectroscopic evidence was found for the presence of the azine cation radical in reaction solutions, but $(Ph_2C\dot{:}CPh_2)^{+\bullet}$ could not be detected. A different, transient e.s.r. spectrum observed at low temperatures consisting of five groups each of seven lines was assigned to $Ph_2CN_2^{+\bullet}$, and a more stable five-line spectrum was observed on oxidation of the related 9-diazofluorene (FlN_2).

In this paper we extend our studies of e.t.c. catalysis to FlN_2, examining the kinetics and products of its decomposition induced electrochemically at a platinum anode and by the chemical oxidants $Cu(BF_4)_2$ or $(p\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$. In conjunction with these experiments, the oxidation of the diazoalkane has been investigated using two transient

electrochemical techniques, linear sweep voltammetry and derivative cyclic voltammetry, to probe the kinetics of the processes which immediately follow the generation of $FlN_2^{+\bullet}$. This combination of kinetic techniques yields mechanistic information on different time scales, and it is shown that significant modification of previous conclusions concerning this type of reaction is necessary.

Results

Reactions induced electrochemically and by $Cu(BF_4)_2$ or $Ar_3N^{+\bullet}SbCl_6^-$.—All experiments were conducted in argon-purged acetonitrile solutions with FlN_2 initially at a concentration of 10^{-2}M. Solutions for electrochemical reactions were saturated with $Me_4N^+BF_4^-$ (ca. 0.07M) and the reactions were conducted at a smooth platinum anode in a divided cell. The progress of all reactions was monitored by i.r. spectrophotometry at 2 050 cm^{-1}. Electrochemical decomposition at low constant current (20 mA; density 0.8 mA cm^{-2}) led to a FlN_2–time curve, showing the sigmoid shape expected[10] of a chain reaction induced by one-electron oxidation (Figure). Confirmation of this was the observation that interruption of the current after ca. 40% reaction led to continued disappearance of the diazoalkane. The principal reaction product was the dimeric olefin bifluorenylidene (Fl=Fl) accompanied by a small amount of fluorenone azine (FlN_2Fl), these two products accounting for almost 99% of the FlN_2 originally present. These two products were also formed in reactions induced by Cu^{2+} or by $Ar_3N^{+\bullet}$ in yields together greater than 95%, but their proportions varied as shown in Table 1.

Examination of the kinetics of the disappearance of FlN_2 in reactions induced by $Cu(BF_4)_2$ or $(p\text{-}BrC_6H_3)_3N^{+\bullet}SbCl_6^-$ ($Ar_3N^{+\bullet}SbCl_6^-$) showed that a first-order law was obeyed with high reproducibility over at least three half-lives. Increase of the catalyst concentration led to a linear increase in the observed rate coefficient (k_{obs}) as shown in Table 2. It seemed necessary that the catalyst be present at concentrations greater than a low
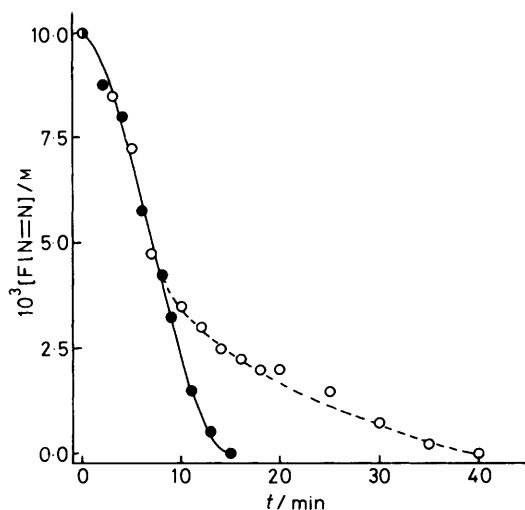
Concentration/time curves for the constant-current electrolysis of FlN_2 ($10^{-2}M$) in CH_3CN–Me_4NBF_4 (sat.) at 30 °C: ● current 20 mA throughout; ○ current (20 mA) stopped after 6 min

Table 1. Products[a] of chemically and electrochemically induced decomposition of FlN_2 in CH_3CN at 30 °C

	Pt Cathode–$Me_4N^+|_4^-$	$Cu(BF_4)_2$	$Ar_3N^{+\cdot}SbCl_6^-$
Fl=Fl	87.4	62.8	34.6
FlN_2Fl	10.9	33.5	63.8
Fl=O	1.3	2.1	1.2
FlHOH	Trace	Trace	Trace
[Fl(OH)]$_2$	Trace	Trace	Trace

[a] % FlN_2 (initially $1.0 \times 10^{-2}M$) converted into each product.

critical value (*ca.* $5.5 \times 10^{-4}M$) if reaction was to go to completion, a finding analogous to that in the case of Ph_2CN_2.[6] Values of k_{obs} fitted equation (1) in the case of $Cu(BF_4)_2$ and (2)

$$k_{obs} = 17.6 \, [Cu(BF_4)_2] - 0.0097 \quad (1)$$

$$k_{obs} = 18.7 \, [Ar_3N^{+\cdot}SbCl_6^-] - 0.0099 \quad (2)$$

in the case of $Ar_3N^{+\cdot}SbCl_6^-$, the similarity of the equations indicating that initial electron transfer from FlN_2 to the catalyst is not rate-limiting since, in acetonitrile, the reduction potentials of the catalysts differ by 0.35 V. In this respect also the behaviour of FlN_2 parallels that of Ph_2CN_2, although the reactivity of FlN_2 is some six times lower.

Voltammetric Studies.—Electrochemical techniques for the study of reactive intermediates in organic reactions have been recently reviewed.[11] In the present work the following techniques were used: derivative linear sweep voltammetry (l.s.v.) in which the effects on the electrode peak potential, E^p, of changes in the voltage sweep rate, v, and substrate concentration are measured; and derivative cyclic voltammetry (d.c.v.) in which the voltage sweep rate is varied so as to hold the observed derivative current ratio R_1' at a predetermined value (usually 0.5) when the substrate concentration is changed. Both techniques permit reaction orders to be determined without resort to detailed calculations, but these are necessary if values for rate coefficients are to be evaluated from d.c.v. results.

The results of the l.s.v. studies on the oxidation of FlN_2 in acetonitrile are in Table 3, from which it can be seen that slopes

Table 2. Kinetics of decomposition of FlN_2 (0.01M) induced by $Cu(BF_4)_2$ and $(p\text{-}BrC_6H_4)_3N^{+\cdot}SbCl_6^-$ in CH_3CN at 30 °C

$10^4[Cu(BF_4)_2]/M$	5.40	6.75	8.10	9.45	10.8
$10^3k_{obs}/s^{-1}$	0.41	1.74	4.8[a]	6.4	9.8
$10^4[Ar_3N^{+\cdot}SbCl_6^-]/M$	6.25	7.50	8.75	10.0	11.25
$10^3k_{obs}/s^{-1}$	1.69	4.6	6.6	9.0[a]	10.9

[a] Invariant on changing $[FlN_2]_0$ by a factor of two: averages of 5—6 values within this range were $(4.78 \pm 0.04) \times 10^{-3} \, s^{-1}$ for $Cu(BF_4)_2$ and $(8.92 \pm 0.08) \times 10^{-3} \, s^{-1}$ for $Ar_3N^{+\cdot}SbCl_6^-$.

Table 3. L.s.v. results for oxidation of FlN_2 in CH_3CN at 22 °C[a]

$[FlN_2]/M$	$dE^p/dlogv/$ (mV)[b]	$v/V \, s^{-1}$	$dE^p/dlog[FlN_2]/$ (mV)[c]
0.125	21.8	0.100	−16.0
0.250	20.5	0.200	−16.5
	(19)[d]		
0.500	20.1	0.400	−17.5
1.00	19.5	1.000	−18.3

[a] Measurements at a Pt anode in CH_3CN containing $Bu_4N^+BF_4^-$ (0.1M). [b] E^p measured at 0.100, 0.200, 0.400, and 1.000 V s^{-1}. [c] E^p measured at $[FlN_2] = 0.125$, 0.250, 0.500, and 1.000 mM. [d] In the presence of pyridine (15.8mM).

$dE^p/dlogv$ and $dE^p/dlog[FlN_2]$ are close to the theoretical values, ± 19.4 mV per decade at 293 K, predicted for a reaction second order in cation radical. There are definite trends in the data, with $dE^p/dlogv$ tending to increase to greater than the theoretical value as the concentration is decreased and $dE^p/dlog[FlN_2]$ tending to lower values as the sweep rate is decreased. These trends can be explained by assuming a competing first-order reaction which becomes more important at low $[FlN_2]$ and low sweep rates, conditions which give rise to lower ion-radical concentrations. No attempt was made to verify this explanation, since the complication is only evident at very low cation-radical concentrations and does not appear to affect the d.c.v. kinetics. A limited number of experiments were carried out in the presence of pyridine which brings on further complications due to electrode filming. It was possible to determine $dE^p/dlogv$ to be close to 19 mV per decade with [pyridine] 16mM. The peak potentials were not significantly changed in the presence of pyridine, which rules out the participation of pyridine in the rate-determining reactions of the cation radicals.

The second-order rate constants for the reaction of $FlN_2^{+\cdot}$ were evaluated from d.c.v. measurements. Because the reaction is so rapid it was necessary to use very high sweep rates (up to 800 V s^{-1}), and low substrate concentrations (as low as 0.05mM) in order to observe the response due to $FlN_2^{+\cdot}$; these factors affect the precision of the measurements. For the same reasons, it was necessary to evaluate derivative peak ratios ranging from 0.2 to 0.35, rather than the typical value of 0.50. Since the theoretical working curves are less steep at the lower values of R_1' this has a further detrimental effect upon the measurement precision. Nevertheless the scatter in the rate constants in Table 4, obtained over a four-fold concentration range, is relatively small and yields an average value of $(1.9 \pm 0.3) \times 10^8 \, l \, mol^{-1} \, s^{-1}$. We are not aware of any report of rate constants for dimerisation of ion radicals as great as this. By extending the voltage range in the d.c.v. experiments, it proved possible to see clearly an oxidation peak which was shown to occur at the same potential as the principal reaction product, bifluorenylidene. While this product signal was most pronounced at sweep rates ranging from 50 to 200 mV s^{-1}, it could still be detected at 1 000 V s^{-1}.

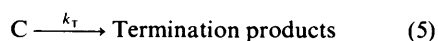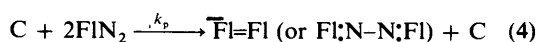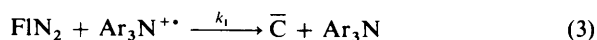**Table 4.** Rate constants for the reaction of 9-diazofluorene cation radical in acetonitrile at 20 °C[a]

[FlN$_2$]/mM	v/V s^{-1}	$10^{-8}k/$ l mol^{-1} s^{-1}
0.050	800	1.5
0.050	600	1.6
0.050	400	2.0
0.050	200	1.6
0.050	100	(1.1)[b]
0.10	800	2.4
0.10	600	1.8
0.10	400	2.1
0.10	200	(1.1)[b]
0.20	800	2.3

Mean 1.9 ($\pm$0.3)

[a] Measurements by derivative cyclic voltammetry. [b] Values excluded from the mean.

Discussion

The kinetic results of the present investigation fall into two distinct groups, the voltammetric ones which refer to events occurring immediately after electron transfer at the electrode and which are very rapid, and the results of macroscopic chemical and electrochemical oxidations which refer to overall chemical change and which occur on a time scale ca. 10^6 times slower. The results of both methods must be incorporated into the overall mechanistic interpretation. It is to be noted at the outset that the different kinetic methods are expected to lead to one-electron oxidation of FlN$_2$ at very different rates. The d.c.v. studies involve the generation of oxidised species close to the electrode in up to millimolar concentrations in times of the order of milliseconds; l.s.v. takes somewhat longer. Electron transfer from FlN$_2$ to Ar$_3$N$^{+\cdot}$, which has an oxidation potential only a few mV less than the diazo compound, can be expected to be complete in a time of the order of a second at the concentrations used here, while in the case of transfer to the less powerful oxidant Cu^{2+} the time might be ca. 100 times longer without the process being observable directly in the present kinetic experiments. Perhaps more crucial, however, is that in d.c.v. the FlN$_2^{+\cdot}$ generated at the electrode surface is exposed to relatively low concentrations of FlN$_2$ during its lifetime, whereas in the chemical oxidations and the preparative electrochemistry FlN$_2$ is in large excess over the cation-radical for most of the course of the reaction.

In its main features the e.t.c.-catalysed decomposition of FlN$_2$ shows a close parallelism with that of Ph$_2$CN$_2$. Thus the products are of the same type and they are produced according to kinetic laws of the same form. A chain process is indicated, which could be as in equations (3)—(5) where C is the chain carrier. Use of the steady-state assumption to derive [C] leads to a kinetic equation which, in order to match the observed kinetic form, would require that (i) the observed rate of disappearance of FlN$_2$ should be proportional to k_1 and (ii) that the rate of propagation should be independent of [FlN$_2$] and that termination should depend on the first power of [C]. We cannot rule out condition (ii) a priori, but condition (i) does not appear

$$\text{FlN}_2 + \text{Ar}_3\text{N}^{+\cdot} \xrightarrow{k_1} \overline{\text{C}} + \text{Ar}_3\text{N} \tag{3}$$

$$\text{C} + 2\text{FlN}_2 \xrightarrow{k_p} \overline{\text{Fl=Fl}} \text{ (or Fl:N-N:Fl) } + \text{C} \tag{4}$$

$$\text{C} \xrightarrow{k_T} \text{Termination products} \tag{5}$$

to hold since Cu^{2+} and Ar$_3$N$^{+\cdot}$ lead to observed rates of disappearance of FlN$_2$ that are the same within experimental error. It would seem then that, on the macroscopic scale, the propagation of the chain is the rate-determining step of the reaction, with initiation fast and termination unimportant above the critical catalyst concentration. The propagation step thus appears to involve FlN$_2$ and the carrier C whose concentration is equal or proportional to the concentration of the oxidant.

Under the conditions of the voltammetric experiments, the results point to dimerisation of FlN$_2^{+\cdot}$. While the d.c.v. results could be interpreted either on this basis or in terms of reaction of FlN$_2^+$ with a second molecule of FlN$_2$, the l.s.v. data make it clear that FlN$_2^{+\cdot}$ is consumed in a process second order in FlN$_2^{+\cdot}$. Moreover, the reaction is very rapid. The fate of all the resultant dimers cannot be ascertained under the experimental conditions, but a significant proportion appears to be converted very rapidly into bifluorenylidene in view of the oxidation peak observed at the appropriate potential even at rapid scan rates. Furthermore, since this product is present in the neutral (i.e., reduced) form, rapid electron transfer, presumably from a further molecule of substrate probably occurs. The time, scale of these events is of the order of milliseconds and certainly very much faster than the rate of product formation on a macroscopic scale.

We conclude therefore that, on the macroscopic scales the chain mechanism which we observe is a different pathway from that detected voltammetrically since, if FlN$_2^{+\cdot}$ dimerised, products would be formed very much more rapidly than is observed. We believe that FlN$_2^{+\cdot}$ must undergo a reaction other than dimerisation and the most obvious one is reaction with FlN$_2$ which, except under the voltammetric conditions, is present in considerable excess over FlN$_2^{+\cdot}$. In order to compete with dimerisation, the reaction of FlN$_2^{+\cdot}$ with FlN$_2$ would have to be more rapid, and it is clear therefore that this step cannot be the rate-limiting one on the macroscopic scale as was suggested for oxidation of Ph$_2$CN$_2$.[6] Indeed, in order to be slow enough to match the observed rates, the reaction must be between FlN$_2$ and a species which is not a powerful enough oxidising agent to convert the substrate into FlN$_2^{+\cdot}$ rapidly by direct transfer of an electron, although it could be in unfavourable equilibrium with such a species. Thus, the product of reaction of FlN$_2^{+\cdot}$ and FlN$_2$ cannot be either (Fl=Fl)$^{+\cdot}$ or (FlN$_2$Fl)$^{+\cdot}$, the radical-cations of the observed reaction products, since both are more powerful oxidising agents than FlN$_2^{+\cdot}$ and would be expected to abstract an electron from FlN$_2$ at a diffusion-controlled rate. Some other species must be involved and this, in all probability, incorporates two fluorenylidene moieties and is a radical.

It may be recalled that reaction of FlN$_2$ with one-electron oxidising agent has previously been reported[6] to give rise to a relatively stable species capable of e.s.r. detection and showing features attributable to coupling of its odd electron with two magnetically equivalent (or nearly so) nitrogen nuclei. We have previously suggested that this spectrum could be that of FlN$_2^{+\cdot}$. Such a view is now clearly untenable, and the spectrum must be assigned to a radical of different structure.* Nevertheless, we believe that it could be a chain carrier and that the rate-limiting step in the chain process is probably reaction of this species, whose concentration is equivalent to that of the oxidising agent, with a molecule of FlN$_2$ by electron transfer. We have at present insufficient information, either kinetic or spectroscopic, to define its structure more closely, but structures (1) and/or (2), radical-cations of 1,1-diazenes,[12] might be

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* Likewise, on the basis of voltammetric studies of the lifetime of Ph$_2$CN$_2^{+\cdot}$, we can no longer assign the 5 × 7-line spectrum observed on oxidising Ph$_2$CN$_2$ at low temperatures to this species.

N•
‖
N
Fl⁺Fl
N≡N

(1)

N•
‖
N
+
Fl——Fl

(2)
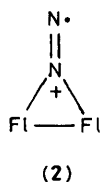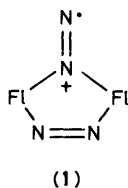
possibilities, provided that such species are relatively poor oxidants. On the other hand, in the absence of knowledge of the radical concentrations at the end of the macroscopic reactions, it remains possible that the e.s.r. signals arise from stable by-products.

Experimental

Materials.—Acetonitrile (Fluka, puriss. p.a.) was dried by passage though a column of activated alumina immediately before use. FlN_2 was prepared by Staudinger's method[13] and after recrystallisation from benzene–light petroleum had m.p. 91 °C (decomp.) and was shown to be free from impurities by h.p.l.c. Pyridine was freshly redistilled.

Preparative Electrolyses.—These were conducted in a thermostatted divided cell fitted with platinum electrodes. The smooth platinum anode had a surface area of 25 cm^2 and was connected to a constant-current generator supplying usually 20 mA. After purging with argon saturated with acetonitrile, the reaction was initiated and samples withdrawn by syringe through a rubber septum. Analysis for FlN_2 was by i.r. spectrophotometry at 2 050 cm^{-1} using a CaF_2 cell which had previously been calibrated with solutions of known concentration.

Kinetic Measurements.—Reactions initiated by $Cu(BF_4)_2$ or $Ar_3N^{+\bullet}SbCl_6^-$ were followed by monitoring the disappearance of the diazo-peak in the i.r. spectrum of samples withdrawn from reaction mixtures. Some scatter of points was observed in the faster reactions due to the fact that the reaction was not quenched in the samples when they were withdrawn.

Product Analyses.—Analyses were mainly conducted by h.p.l.c. using a reversed-phase column (Spectra Physics RP18-2776) and eluting with 85% aqueous acetonitrile. The standard was triphenylethylene. G.l.c. analysis using a 1 m × 0.25 cm stainless steel column containing 5% OV1 on Celite (temperature programme 150—320 °C) was used in a few cases.

Voltammetric Measurements.—LSV measurements were made as described previously.[1] The procedure for d.c.v. measurements has been described previously,[14] and the theoretical data for the evaluation of rate constants have already been reported.[15]

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