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The Multiplicity of Reaction Pathways of Cation Radicals Derived from Anthracene Derivatives in Solvents of Low Nucleophilicity

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In acetonitrile containing trifluoroacetic acid, the cation radicals of 9-substituted anthracenes either dimerize (a), react with acetonitrile (b) or react with trifluoroacetic acid (c) depending on the nature of the 9-substituent. All three reaction pathways were demonstrated during kinetic and product studies. Pathway (a) is of importance when the intermediate dimeric dication, which has both the substituents and the charges in the 10,10′-positions, is stabilized by virtue of the electron donating properties of the substituent. This pathway was observed exclusively for 9-phenyl and 9-methoxy and to a lesser extent when the substituent was 9-chloro. Pathway (c) predominates when the 9-substituent destabilizes the positive charge as is the case for 9-nitro. The intermediate case (b) is the predominant reaction pathway for the anthracene cation radical and is also observed when the substituent is 9-methyl. The feature of pathway (b) which differs most from (c) is that the intermediate cation radical-nucleophile adduct in (b) is charged and if the substituent is electron withdrawing the oxidation of this species by cation radical is less favorable so that trifluoroacetoxylation (c) can then effectively compete. All three of the reaction pathways were observed to give rise to complex rate laws.

The reactions of the cation radicals of anthracene and substituted anthracenes have been the subject of numerous investigations.[1–45] The reactions usually produce easily characterized products and this has contributed to their use as model substrates. The first indication of the mechanism of anodic substitution emerged from the study of the anodic pyridination of anthracene[1] in which it was observed that the two-electron oxidation of anthracene in acetonitrile in the presence of pyridine was accompanied by the formation of the 9,10-dipyridinium salt. The oxidation of anthracene in acetonitrile containing water was later shown to produce 10,10′-bianthronyl in high yield.[2] The mechanism of this reaction was suggested to involve the reaction of the cation radical with water to give anthrone as the first product which then undergoes air-oxidation during the work-up procedure.[3] Coulometric and products studies[12–14] later showed that anthrone is not an intermediate in the reaction of the cation radical with water and that 10,10′-bianthronyl is the first stable reaction product. Detailed studies were carried out on several reactions of anthracene cation radical including hydroxylation,[15] acetoxylation[16] and methoxylation.[17]

The anthracenes, particularly 9,10-diphenylanthracene (DPA), served as essential substrates to establish the one-electron oxidation pathway of aromatic hydrocarbons in aprotic media. The latter was firmly established by three independent studies in different solvent systems including acetonitrile,[4] dichloromethane[5] and nitrobenzene.[6] The first definitive kinetic studies of the reactions of cation radicals employed DPA as substrate for hydroxylation[7] and pyridination.[9] The so-called "half-regeneration" and ECE mechanisms, were proposed for these reactions, both of which involve the cation radical as the intermediate reacting with the nucleophile. However, it was later observed that chronoamperometric data for the pyridination of

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DPA were more consistent with the theoretical working curve for the disproportionation mechanism than with that for the ECE scheme, an observation which suggested that the dication is the reactive intermediate.[21]

The mechanism dispute, *i.e.* cation radical (eqn. (1))[9] or dication (eqn. (2))[21] was at about the same time emerging for a related reaction, that of thiantrene cation radical with water.[46,47] These two

$$A^{\cdot+} + N \rightarrow A^{\cdot} - N^{+} \quad (1)$$

$$A^{2+} + N \rightarrow A^{+} - N^{+} \quad (2)$$

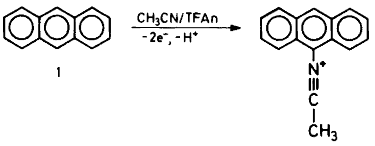
systems and the important mechanistic distinction between primary reactions (1) or (2) set the stage for most of the mechanistic studies of cation radical reactions which were carried out in the 1970's. The proposal of the disproportionation mechanism for the pyridination of $DPA^{\cdot+}$ was shown to be highly unlikely by a kinetic analysis taking into account the small value of the disproportionation equilibrium constant (K_3).[23] It was shown that forward reaction (3) would limit the rate of

$$2\,DPA^{\cdot+} \overset{K_3}{\rightleftharpoons} DPA^{2+} + DPA \quad (3)$$

the overall reaction leading to kinetics independent of the pyridine concentration[23] which is contrary to the experimental observations.[9] The need for reliable data to estimate disproportionation equilibrium constants led to the development of methods to determine the reversible potentials for the oxidation of cation radicals to dications,[26] a highly useful benefit resulting from the mechanism controversy.

Spectroelectrochemical studies,[32,33] apart from minor differences, confirmed the conclusions on the mechanism of the hydroxylation of $DPA^{\cdot+}$. Homogeneous kinetic studies[29,36,37] and spectroelectrochemical[28,36] investigations confirmed the earlier conclusion[9,23] that the cation radical is the reactive intermediate involved in the pyridination of $DPA^{\cdot+}$. Similarly, the much more reactive cation radical derived from 9-phenylanthracene was observed to react with pyridine with a rate constant of the order of 10^7 M^{-1} s^{-1} at 298 K.[49] A number of other nucleophiles have been employed but as yet there is not general agreement on the detailed mechanism of any of the reactions.[43,48]

In a preliminary communication[27] on which this work is based, we observed that when water is effectively removed from acetonitrile solutions anthracene cation radical reacts with solvent to give the nitrilium ion (eqn. (4)). The purpose of this paper is to outline the reaction pathways of cation radicals of anthracene and 9-substituted anthracenes in media with only weak nucleophiles present.

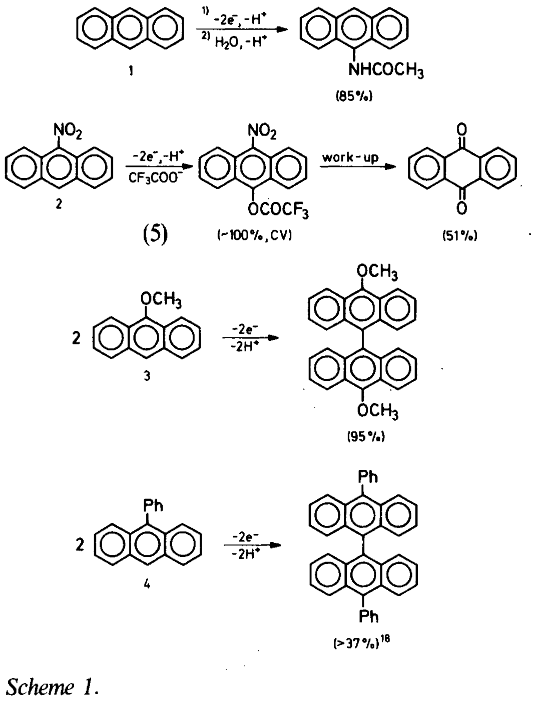


(4)

RESULTS

Product studies. The results of preparative anodic oxidation of anthracene, *1*, and different 9-substituted anthracenes demonstrated that essentially three different reaction pathways were followed dependent on the nature of the substituent as illustrated in Scheme 1. Formation of the acetamido derivative was the major reaction for *1* and was also observed for 9-methyl- and 9-chloroanthracene, although to a lesser extent (30 – 40 %).

In the case of 9-nitroanthracene, *2*, an apparent inconsistency between the results obtained by cyclic



Scheme 1.

voltammetry and preparative electrolysis was observed. CV analysis demonstrated (see next section) the product to be 9-nitro-10-trifluoroacetoxyanthracene, while the product isolated after preparative electrolysis was found to be anthraquinone. However, it is most likely that the anthraquinone does arise *via* the trifluoroacetoxy derivative which may suffer hydrolysis during work-up in a process similar to the Nef reaction. When the 9-substituent was either methoxy, *3*, or phenyl, *4*, the isolated products were dimers resulting from coupling reactions. The dimers were further oxidized under the reaction conditions which may cause the isolated yield to be low if irreversible follow-up reactions can take place as was observed in the case of *4*. The earlier result[18] that higher oxidation products of the dimer were formed during electrolysis was confirmed in this study. The 10,10′-dimer could be detected as a minor product from 9-chloroanthracene as well.

Trifluoroacetoxylation of 9-nitroanthracene. In acetonitrile containing trifluoroacetic acid and trifluoroacetic anhydride (AN–TFA–TFAn = 9:1:1) cyclic voltammetry indicated not only the primary oxidation peak but also one due to the oxidation of a reaction product of the cation radical. In the presence of $CF_3CO_2^-LH^+$ (L = 2,6-lutidine), prepared *in situ* by the reaction of TFA with L, the peak due to the reaction product was about the same height as the primary peak indicating nearly complete reaction when the voltage sweep rate (v) was 200 mV/s. Derivative cyclic voltammograms for the solution containing $CF_3CO_2^-LH^+$ (44 mM) with v equal to 200, 2.00 and 0.200 V/s are illustrated in Fig. 1. At 200 V/s (a), the peak due to the reaction product O'_2 is approximately half as intense as that due to the oxidation of substrate O'_1 and the peak due to the reduction of the cation radical derived from substrate, R'_1, is observed on the reverse scan. At 2.00 V/s (b) reaction between the cation radical and $CF_3CO_2^-$ is nearly complete during the time scale of the measurement and the CV peak potentials for oxidation of substrate and the trifluoroacetoxy derivative were observed to be 1.415 and 1.640 V *vs.* $Ag/Ag^+(CH_3CN)$. At $v = 0.200$ V/s (c), O'_2 is slightly more intense than O'_1 indicating complete reaction. In analogy with earlier work on the reaction of $4^{\cdot+}$ with nucleophiles,[11,20] it can be deduced from the voltammograms that the product arises from substitution reaction (5) rather than addition of two $CF_3CO_2^-$. The addition reaction gives rise to a derivative in which the central ring is saturated and is not oxidized in the potential range of the experiment.[11,20]

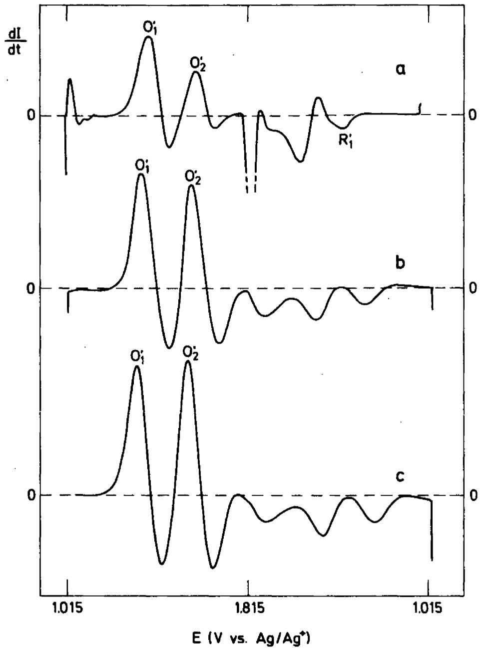


Fig. 1. Derivative cyclic voltammograms for the oxidation of 9-nitroanthracene in acetonitrile–TFA–TFAn (9:1:1) containing $CF_3CO_2^-$ (44 mM) and supporting electrolyte, Bu_4NBF_4 (0.1 M). Voltage scan rates: 200 V/s (a), 2 V/s (b) and 0.2 V/s (c). Switching potential: 1.815 V.

Kinetic studies. Derivative cyclic voltammetry (DCV)[50,51] kinetic studies were carried out on the reactions of the cation radicals derived from *1*, *2* and *4*. The data were treated according to procedures[52] which have been summarized in a recent paper.[53]

The data in Table 1 illustrate the effect of substrate concentration (C_A) and temperature on the apparent

Table 1. DCV kinetic study of the reaction of anthracene cation radical with acetonitrile in AN–TFAn (9:1).

C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_A^{0.5}$	T/K
0.25	12.8	810	293.2
0.50	19.3	863	293.2
1.00	28.3	895	293.2
0.50	38.4	–	273.2

Table 2. DCV kinetic study of the reaction of anthracene cation radical with trifluoroacetate ion.[a]

C_A/mM	$C_{CF_3CO_2^-}$/mM	$v_{\frac{1}{2}}$/V s^{-1}	$(v_{\frac{1}{2}}/C_{CF_3CO_2^-}) \times 10^{-3}$
0.313	0	24.6	–
0.313	4.15	44.0	10.6
0.313	8.30	72.2	8.70
0.313	16.6	135.9	8.19
1.25	0	50.0	–
1.25	4.15	93.6	22.6
1.25	6.23	138.3	22.2
1.25	8.30	160.0	19.3
1.25	16.6	217.9	13.1

[a] Measurements at 293.2 K in acetonitrile – TFAn (9:1) containing TFA (5 %).

rate constant for the reaction of $1^{\cdot +}$ with acetonitrile as reflected by $v_{\frac{1}{2}}$, the voltage sweep rate at which the derivative peak ratio is equal to 0.500.[52] The reaction order, $R_{A/B}$, which reflects the contributions of both the primary intermediate B ($1^{\cdot +}$ in this case) and the substrate A (1 in this case) is given by eqn. (6) and the third column in Table 1 shows that

$$R_{A/B}=1+z \quad (v_{\frac{1}{2}}/C_A^z=\text{constant}) \qquad (6)$$

a good fit of the data to (6) is obtained for $z=0.5$ and $R_{A/B}=1.5$. A comparison of the data in the second and fourth columns provides evidence of a complex mechanism for the reaction with a 20 K decrease in temperature giving rise to a doubling in the apparent rate of the reaction. The mechanistic implications of inverse temperature effects in ion radical reactions have recently been discussed.[54]

The apparent rate constant for the reaction of $1^{\cdot +}$ in AN – TFA – TFAn (9:1:1) was observed to be increased by the presence of $CF_3CO_2^-LH^+$. The last column in Table 2 shows that the reaction order in the salt is very nearly 1 at two different substrate concentrations. At both C_A the rate increased by about a factor of 5 on going from C_{salt} of 0 to 16.6 mM. The temperature dependence of the apparent rate constant (Table 3) was observed to be approximately the same as in the absence of the salt (Table 1) with nearly a two-fold increase accompanying a 20 K temperature decrease.

Table 3. Effect of temperature on the reaction of anthracene cation radical with trifluoroacetate ion.[a]

T/K	$v_{\frac{1}{2}}$/V s^{-1}
293.2	135.5
282.9	203.5
273.2	261.2

[a] In acetonitrile – TFAn (9:1) containing TFA (5 %) and $CF_3CO_2^-$ (16.6 mM).

The rate of decomposition of $2^{\cdot +}$ in AN – TFAn (9:1) was very low in the absence of TFA. The lifetime of the cation radical was greatly decreased in the presence of TFA and the rate of decomposition was observed to be significantly increased in the presence of $CF_3CO_2{}^-LH^+$. The last column in Table 5 is indicative that at two different substrate concentrations the reaction order in $CF_3CO_2{}^-$ is 1. This relationship does not hold at low salt concentrations at C_A equal 1.00 mM. Apparent activation energies were obtained from $v_{\frac{1}{2}}$ measured over a 20 K temperature range at C_A equal 0.25 and 1.00 mM (Table 6) using the relationship reported recently[55] which does not require the evaluation of rate constants. Values of 7.6 kcal/mol ($r=-0.997$) and 7.3 kcal/mol ($r=-0.989$) were observed at 1.00 and 0.25 mM, respectively.

Table 4. DCV kinetic study of the reaction of 9-nitroanthracene cation radical with trifluoroacetate ion in acetonitrile – TFAn (9:1).[a]

C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_A^{-0.75}$
0.25	180	0.358
0.50	117	0.391
0.75	90.5	0.410
1.00	60.0	0.337
		0.374±0.033

[a] Measurements at 280.4 K in solvent containing TFA (5 %) and $CF_3CO_2^-$ (8.3 mM).

Table 5. DCV kinetic study of the reaction of 9-nitroanthracene cation radical with trifluoroacetate ion at different concentrations.[a]

C_A/mM	$C_{CF_3CO_2^-}$/mM	$v_{1/2}$/V s^{-1}	$(v_{1/2}/C_{CF_3CO_2^-})\times 10^{-3}$
0.25	0	21.0	–
0.25	4.15	101.5	24.5
0.25	6.23	145.4	23.3
0.25	8.30	201.5	24.3
1.00	0	3.7	–
1.00	4.15	9.0	2.17
1.00	8.30	88.8	10.7
1.00	12.45	136.4	11.0
1.00	16.6	179.3	10.8

[a] Measurements at 292.1 K.

Table 6. Effect of temperature on the reaction of 9-nitroanthracene cation radical with trifluoroacetate ion.[a]

C_A/mM	T/K	$C_{CF_3CO_2^-}$/mM	$v_{1/2}$/V s^{-1}
1.00	293.5	16.6	229.7
1.00	281.7	16.6	136.2
1.00	273.2	16.6	80.8
0.25	292.1	8.3	201.5
0.25	282.7	8.3	114.5
0.25	273.2	8.3	78.8

[a] Measurements in acetonitrile–TFAn (9:1) containing TFA (5 %).

Table 7. DCV kinetic study of the reaction of 9-phenylanthracene in acetonitrile–TFAn (9:1).[a]

C_A/mM	$v_{3/4}$/V s^{-1}	$v_{3/4}/C_A$	T/K
0.50	0.133	266	287.5
1.00	0.269	269	287.5
1.50	0.433	289	287.5
2.00	0.481	241	287.5
2.00	0.525	–	273.2
2.00	0.542	–	303.4

[a] Measurements in solvent containing TFA (5 %) and $CF_3CO_2^-$ (8.3 mM).

Data obtained over an eight-fold range of C_A indicate that $R_{A/B}$ for the reaction of *4*$^{\cdot +}$ in AN–TFA–TFAn (9:1:1) in the presence of $CF_3CO_2^-LH^+$ (8.3 mM) is very close to 2 (Table 7). Because of the low rate of reaction in this case, $v_{3/4}$, the sweep rate necessary for the derivative peak ratio to equal 0.750 was used instead of $v_{1/2}$. At three temperatures $v_{3/4}/T$ was very nearly constant which indicated an apparent activation energy close to 0.

Linear sweep voltammetry studies. Linear sweep voltammetry studies were carried out on the reactions of *1*$^{\cdot +}$ and *2*$^{\cdot +}$. The data in Table 8 can be analyzed using eqns. (7) and (8) where the lower case letters refer to reactions orders in A (*a*), and B (*b*).[56] In AN–TFAn (9:1) the reaction order in *1*$^{\cdot +}$ was

$$dE^p/d\log v = [1/(b+1)](\ln 10)RT/nF \qquad (7)$$

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

very close to 2 and that in *1* was −1 within experimental error. The theoretical values at 19.3 °C are 19.3 and 0 mV/decade for $dE^p/d\log v$ and $dE^p/d\log C_A$, respectively. The data for the reaction of *1*$^{\cdot +}$ in the presence of $CF_3CO_2^-$ are most consistent with eqns. (7) and (8) when $b=1.7$ and $a=0$. The latter

Table 8. Linear sweep voltammetry kinetic analysis of the reactions of anthracene cation radicals.

Substrate	Conditions	$dE^p/d\log v$	$dE^p/d\log C_A$
Anthracene	*a*	18.4 (0.1)	−0.7 (3.6)
Anthracene	*b*	21.3 (1.2)	−13.5 (0.7)
9-Nitroanthracene	*b*	28.0 (1.7)	+2.3 (2.1)

[a] Acetonitrile–TFAn (9:1) at 292.5 K. [b] Acetonitrile–TFAn (9:1) containing TFA (5 %) and $CF_3CO_2^-$ (8.3 mM) at 292.5 K.

result is arrived at by first solving for b in eqn. (7) and then checking eqn. (8) for consistency. The data in the third row of Table 8 indicate that within experimental error, $a=0$ and $b=1$ in the rate law describing the reaction of $2^{\cdot+}$ in AN–TFA–TFAn (9:1:1) containing $CF_3CO_2^-$ (8.3 mM).

DISCUSSION

At the outset of this investigation it was our intention to study the effect of substituents in the 9-position of the anthracene nucleus on the kinetics of the acetamidation of the cation radicals. However, our preliminary results indicated that no two ion radicals in this series undergo precisely the same reactions. We were especially surprised to find what appeared to be an inverse stability–reactivity relationship in that in the absence of added nucleophiles, 9-nitroanthracene cation radical reacts very slowly in AN–TFAn (9:1) while anthracene cation radical is moderately reactive. Our preliminary report on the reaction of anthracene cation radical with acetonitrile[27] naively assumed, as was common to investigations at that stage in the development of ion radical chemistry, that the observed rate constant was a measure of the microscopic rate constant for the first step of reaction (4). More recent work has provided ample evidence that even those reactions which have long been considered to follow simple mechanisms, such as hydrodimerization of anion radicals,[57–60] formation of stable dimer dianions of anion radicals,[61] deprotonation of methylarene cation radicals,[54,62] and the protonation of aromatic hydrocarbon anion radicals[63,64] as well as the pyridination of 9,10-diphenylanthracene cation radical,[43,48] are in fact very complex. With this background, it is perhaps not very surprising to find that a not so subtle change in structure as the nature of the 9-substituent can give rise to an apparent complete change in mechanism of the reaction of cation radicals of substituted anthracenes.

However, we will attempt to show that a manifold of equilibria in which all of the cation radicals can participate is adequate to explain the differences in the products observed. The substituents can be expected to exert their influence on the magnitudes of the various equilibrium constants.

The product studies indicate that the overall reaction pathways can be categorized as dimerization (a), acetamidation (b) and trifluoroacetoxylation (c). The kinetic studies revealed that the rate laws for the reactions of all of the cation radicals are complex and that the evaluation of rate constants is somewhat superfluous in that in no case can a rate constant be assigned to any one microscopic step.

As a starting point, we can consider what appears to be the most simple case encountered, *i.e.* the dimerization of 9-phenylanthracene cation radicals. The kinetic data (Table 7) are consistent with rate law (9). Cation radical dimerization has been observed to have an appreciable activation energy in related cases[65] which suggests that k_{app} in rate law (9) does not apply to the simple irreversible

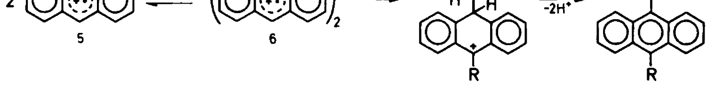
$$\text{Rate}=k_{app}[4^{\cdot+}]^2 \tag{9}$$

conversion of *5* to *7* (pathway (a)) but rather to the preequilibrium defined by $K_{5,6}$ followed by rate determining $k_{6,7}$ since an apparent activation energy of about 0 was observed for this reaction. Precisely the same situation has been encountered in the dimerization of anion radicals derived from 9-substituted anthracenes[61] and 9-diazofluorene.[66] It is of interest that the dimerization takes place in the presence of the moderately good nucleophile, trifluoroacetate ion.

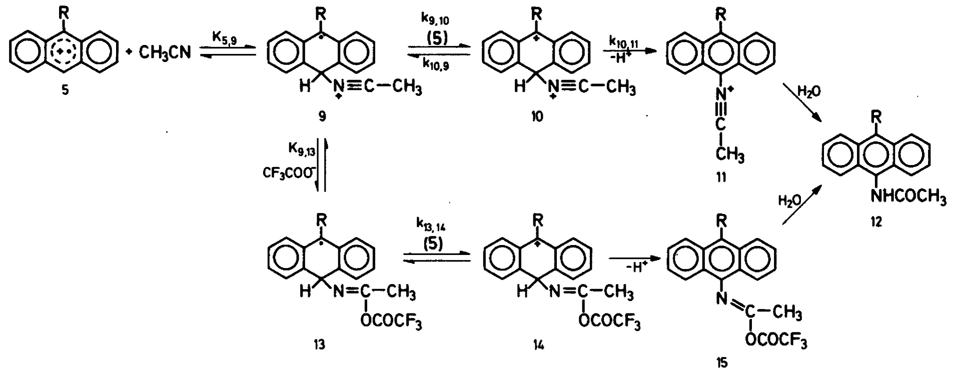
There are a number of noteworthy features of the kinetic data for the acetamidation of anthracene cation radical. In AN–TFAn (9:1), reaction orders in $1^{\cdot+}$ and 1 were observed to be 2 and –1, respectively, (Table 8), which is indicative of rate law (10). In the presence of $CF_3CO_2^-$, there appears to

$$\text{Rate}=k_{app}[1^{\cdot+}]^2/[1] \tag{10}$$

be a competing first order reaction and the order in *1* goes to 0. These results must be considered in



Pathway a



Pathway b

conjunction with the DCV study (Table 2) which indicates a reaction order of 1 for $CF_3CO_2^-$. The kinetic data can be accounted for by pathway (b). Rate law (10) can be explained by equilibria with constants $K_{5,9}$ and $K_{9,10}$ $(=k_{9,10}/k_{10,9})$ followed by rate determining step $k_{10,11}$ with $k_{app}=K_{5,9}K_{9,10}k_{10,11}$. In the presence of $CF_3CO_2^-$ the reaction is second order in cation radical consistent with rate law (11). This rate law is satisfied by

$$\text{Rate}=k_{app}[1^{\cdot+}]^2[CF_3CO_2^-] \qquad (11)$$

pathway (b) when $k_{app}=K_{5,9}K_{9,13}k_{13,14}$. The catalytic effect of $CF_3CO_2^-$ can be accounted for by the production of neutral *13* which is more easily and rapidly oxidized by *5* than is the cation radical *9*. The inverse temperature effect (Tables 1 and 3) which is the same in the presence or absence of $CF_3CO_2^-$ could mainly be due to the effect of temperature on $K_{5,9}$.

The DCV data in Table 1 were obtained under similar conditions where rate law (10) was observed by LSV (Table 8). This is not an inconsistency. A different regime of cation radical concentrations prevails in the two types of experiments. The data in Table 1 are consistent with rate law (12), differing only from (10) in that back-reaction with $k_{10,9}$ takes place at a rate similar to that with rate constant $k_{10,11}$. The competing reaction which is first order in $1^{\cdot+}$ is most likely the reaction of the cation radical with $CF_3CO_2^-$(pathway (c)) discussed

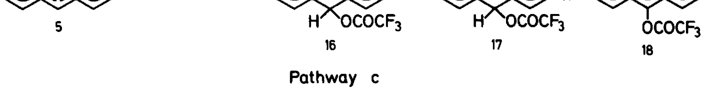
$$\text{Rate}=k_{10,11}K_{5,9}[1^{\cdot+}]^2/(k_{10,9}[1]+k_{10,11}) \qquad (12)$$

below.

The LSV study of the reaction of 9-nitroanthracene cation radical with $CF_3CO_2^-$ provides the strongest evidence for reaction pathway (c) and rate law (13). The reaction order in $CF_3CO_2^-$

$$\text{Rate}=k_{5,16}[2^{\cdot+}][CF_3CO_2^-] \qquad (13)$$

was derived from the DCV data (Table 5). The apparent activation energy of about 7.5 kcal/mol is also consistent with the effect of temperature on $k_{5,16}$. But here we encounter another apparent inconsistency. The data in Table 4 show a remarkable decrease in rate as the substrate concentration is increased. This can be explained by the formation of an inhibitor during the reaction. The only possible inhibitor in pathway (c) is the proton generated in the last step. However, this explanation is not compatible with the observation of rate law (13) in other experiments. An explanation consistent with the entire series of equilibria giving rise to the three pathways is that $2^{\cdot+}$ exists as a dimer complex as *6* or that it associates strongly with substrate. Both of these equilibria are known to be important for related cation radicals.[67] Because of



Pathway c

the presence of electron withdrawing nitro, association with substrate which gives rise to spreading the positive charge over two molecules would be especially favorable. In fact the equilibrium constant for the latter reaction has been observed to be about two orders of magnitude greater than that for cation radical association in some cases.[67] Reaction pathway (c) requires that the dimer dissociate to the reacting intermediate *5*. The importance of the side equilibrium is enhanced as the concentration of substrate is increased giving rise to the low value of $R_{A/B}$, 0.25 (Table 4), observed.

The specific influence that a particular substituent has on which of the three reaction pathways will predominate remains to be explained. Pathway (a) predominates or is followed exclusively when the 9-substituent is either phenyl or methoxy. Both of these substituents strongly stabilize the positive charges in the 10,10′-positions of the dimer dication *7*.

The discussion in the previous paragraph led to the conclusion that when the 9-substituent is nitro the pre-equilibrium complex *6* may be formed. It is clear that nitro substituents in the 10,10′-positions of *7* will strongly destabilize that structure which prevents pathway (a) from taking place in that case. The reason that the 9-nitro substituent prevents reaction with acetonitrile is also readily explained. The homogeneous electron transfer reaction by which *9* is converted to *10* is expected to be less favorable when R is electron withdrawing NO_2. On the other hand, intermediate *16* is expected to be more easily oxidized than cation radical *9* which allows pathway (c) to channel the 9-nitroanthracene cation radical reaction leading to the trifluoroacetate *18*.

EXPERIMENTAL

The instrumentation, data handling procedures, cells, electrodes and solvent and supporting electrolyte purification were the same as recently described.[43] Anthracene (Fluka, *purum*), 9-nitroanthracene (Fluka, *purum*), 9-phenylanthracene (EGA-Chemie, 98 %) and 9-methylanthracene (EGA-Chemie, 99 %) were used as received. 9-Chloroanthracene[68] and 9-methoxyanthracene[69] were prepared by standard procedures.

Preparative electrolyses. Substrate (1.0 mmol) was dissolved or suspended in acetonitrile – TFAn (40 ml, 9:1) containing Bu_4NBF_4 (0.2 M) and subjected to constant current (100 mA) oxidation for the calculated amount of time (16.1 min for 1 F/mol and 32.2 min for 2 F/mol). The cell was a Metrohm titration vessel, model EA 876, and a sintered glass disk (G 3) served to separate the anolyte and the catholyte (AN/TFAn, 10 ml, 9/1). Electrodes were platinum gauzes. The electrolysis mixture was poured onto crushed ice (~ 150 g) and stirred for 15 min. The resulting solution was extracted with diethyl ether (4 × 40 ml) and the combined organic phases were washed with water (3 × 40 ml) which caused the supporting electrolyte to precipitate. The solid material was removed by filtration and the resulting solution was dried over Na_2CO_3. The solvent was removed at reduced pressure. Yields were determined by GLC (OV 1, 3 %) and the identity of the products was confirmed by comparison with authentic samples.

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