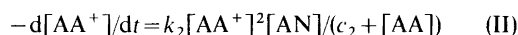
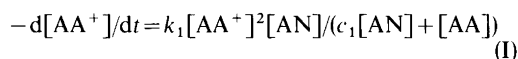


Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. VII.* Competing Second Order Reactions during the Anisylation of the 9-Anisylanthracene Cation Radical

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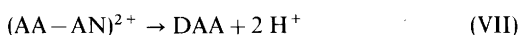
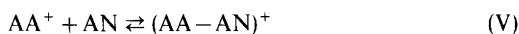
The cation radical of 9-anisylanthracene (AA) reacts with anisole (AN) to form 9,10-dianisylanthracene (DAA) in high yield along with an equimolar amount of AA. In the presence of excess AN and AA, the reaction was found to be second order in [AA⁺]. Studies of the effect of [AA] and [AN] on the pseudo second order rate constant (k_{obs}) revealed that the reaction was taking place by two competing mechanisms with rate laws (I) and (II)



Rate law (I) is due to the disproportionation mechanism (III+IV) while rate law (II) results



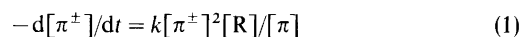
from the complexation mechanism (V–VII)



At high [AN] the complexation mechanism was found to predominate while at low [AN] disproportionation was nearly the exclusive reaction path-

way. This is the expected effect considering that [AN] appears in the denominator of the disproportionation rate law (I). The overall rate constant (k_{obs}) could be calculated from the expected contributions due to the two mechanisms, the rate constants for which were evaluated at different [AN], giving good agreement with the observed rate constants.

Kinetic studies of the reactions of radical ions often reveal rate laws second order in the radical ion.^{1,2–6} For the reaction of a radical ion with a reagent, R, a frequently observed rate law is (1). The observation of (1) is then often taken as evidence for the disproportionation mechanism (eqns. 2+3).^{2–6} The symbol, π , refers to an aromatic compound.



The application of a combination of equilibrium and steady state approximations⁷ to the disproportionation mechanism reveals that the complete rate law is (4) which reduces to (1) only under special conditions. When reverse reaction (2) is energetically favored, k_3 is expected to be large, *i.e.* 10^6 – 10^{10} $\text{M}^{-1} \text{s}^{-1}$ [eqn. (4)]. Aromatic dications as well as

* Parts I–VI, see Ref. 1.

$$-d[\pi^\pm]/dt = 2k_3k_2/k_{-2}[\pi^\pm]^2[R]/(k_3/k_{-2}[R] + [\pi]) \quad (4)$$

dianions are very reactive species and thus reactions (3) are expected to have large rate constants. For example, recent direct measurements on the protonation rates of perylene and anthracene dianions by methanol gave rate constants of 10^5 and 10^7 $M^{-1} s^{-1}$, respectively,⁸ in good agreement with estimates based on assuming the disproportionation mechanism.^{5,6} Thus, it is reasonable to expect the magnitude of k_3/k_{-2} to be of the order 10^{-4} to 1.0 in most cases of interest. The latter being the case, it is readily seen that the relative importance of the two terms in the denominator of (4) can be changed by adjustment of the concentrations of R and π . Under conditions where the two terms have values of the same order of magnitude, the disproportionation mechanism predicts a reaction order less than unity in [R] and less negative than -1 in $[\pi]$. Obviously, the demonstration of these relationships is far better evidence for the disproportionation mechanism than the mere observation of a second order dependence of the reaction rate on radical concentration. Unfortunately, adequate attempts to observe rate law (4) are rare.

We have recently observed that the cation radicals of the aromatic hydrocarbons, 9-phenylanthracene and anthracene, react with a variety of aromatic compounds to give the arylated products in high yield.¹⁶ We have now observed the same type of reaction between 9-anisylanthracene (AA) cation radical and anisole (AN). Here we report a kinetic study of the latter reaction. The reactions were carried out in solvent systems containing trifluoroacetic acid (TFA) and trifluoroacetic acid anhydride (TFAn) which have recently been shown to be very effective in rendering aprotic solvents sufficiently free of nucleophiles so as to allow for the preparation of stable solutions of aromatic cation radicals.^{9,10} The kinetic study of the reaction of AA⁺ with AN led to the rewarding result that although two mechanisms are operative, the pro-

portion of the reaction following one or the other mechanism can be changed by changes in [AN]. Evidence is presented which strongly implies disproportionation as one of the competing reaction pathways.

RESULTS

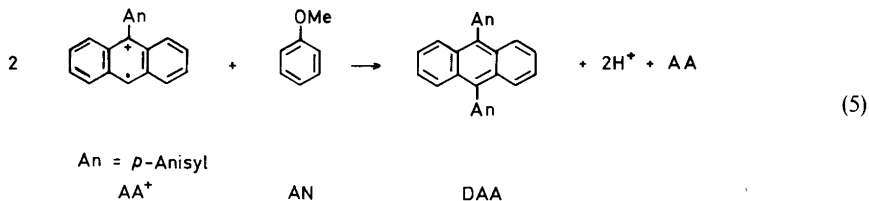
The reaction of AA⁺ with AN was observed to follow the stoichiometry of the half generation reaction (5), *i.e.* two equivalents of the cation react to give DAA and AA. The product (DAA) was identified by comparing the visible spectra of the neutral compound and the corresponding cation radical as well as their voltammetric behaviour to that of the authentic compound.¹¹ A more convenient method for the preparation of DAA was found to be the anodic oxidation of AA in the presence of AN in CH_2Cl_2 -TFA-TFAn (97:2:1) which resulted in near quantitative yields of DAA.

Voltammetric determination of K_{disp} for AA⁺. The difference in standard electrode potentials (ΔE°) for charge transfers from AA to give first AA⁺ and then AA²⁺ at 11 °C in CH_2Cl_2 -TFA-TFAn (97:2:1) was found to be greater than 410 mV. The uncertainty in the value of ΔE° arises from the fact that the oxidation of AA⁺ is irreversible due to a fast reaction of AA²⁺ probably with a component of the solvent system. However, the data allows us to estimate K_{disp} for reaction (6) to be 1.1×10^{-7}



at 11 °C in CH_2Cl_2 -TFA-TFAn (97:2:1).

General comments on the kinetic method and the treatment of data. The method used for obtaining kinetic data has been described for the pyridination of the 9,10-diphenylanthracene cation radical.¹² The procedure involved monitoring the decrease in radical ion concentration at the rotating disc electrode (rde). The stable cation radical was first prepared by the constant current oxidation of AA.



After addition of anisole, the concentration of AA^+ was monitored at a fixed potential about 200 mV more negative than necessary to reduce the cation radical. In general, the reactions were followed for several half lives.

In the presence of TFA, AA^+ reacts according to a second order rate law. This reaction, trifluoroacetoxylation of AA^+ , was only significant at the lowest anisole concentration used. The observed rate constant for trifluoroacetoxylation in CH_2Cl_2 –TFA–TFAn (97:2:1) was found to be equal to about $2 M^{-1} s^{-1}$ at 11 °C. In order to analyze the data for the anisylation reaction, the decrease in $[AA^+]$ due to trifluoroacetoxylation was first taken into account. This was done in every run by measuring the decay in $[AA^+]$ before addition of anisole. After accounting for the loss of AA^+ in this reaction, the data were plotted in accordance with a pseudo second order reaction, *i.e.* $1/[AA^+]$ *vs.* time. Linear plots were obtained for at least one half-life. Deviations from linearity at higher conversions were due to the fact that the product of the overall reaction is DAA^+ which is reduced at the potential where the rde current was measured. In order to further insure that the reaction is second order in $[AA^+]$, the initial $[AA^+]$ was varied over about a factor of 7 with consistent rate constants being obtained.

Analysis of the kinetic data. The reaction between AA^+ and AN is second order in $[AA^+]$ when the reaction is conducted in the presence of excess AA and AN so that the concentrations of

these species do not change significantly during the reaction. The mechanisms shown in Table 1 may account for the second order kinetics. The reaction rate was found to be inhibited by unoxidized AA which is consistent with rate laws (14) and (15) for the complexation and disproportionation mechanisms, respectively. Mechanism C, the dimerization of AA^+ followed by reaction with AN, is described by rate law (16) which does not contain a term for $[AA]$ in the denominator. Thus, mechanism C need not be considered further.

The distinguishing difference between rate eqns. (14) and (15) is the anisole dependence. Rate law (14) shows that the mechanism A predicts a first order dependence in $[AN]$. Providing that $c_{15}[AN]$ is either larger than or of comparable magnitude to $[AA]$, rate law (15) indicates that mechanism B predicts a fractional order in $[AN]$. Thus, at a given $[AA]$, a fractional order in $[AN]$ suggests that the reaction follows, at least in part, the disproportionation mechanism. If disproportionation were the exclusive mechanism, the dependence of the observed rate constant (k_{obs}) at a given $[AA]$ on $[AN]$ is readily predicted. The predicted anisole dependence then gives a test to determine whether or not disproportionation is the sole reaction pathway. The expected effect, under disproportionation conditions, is that k_{obs} should show a decreasing dependence on $[AN]$ as the latter is increased and at sufficiently high $[AN]$ the rate constant should become independent on the anisole concentration.

Table 1. Second order reaction mechanisms of anisylanthracene cation radical.

Mechanism	Rate law
A. Complexation	
$AA^+ + AN \rightleftharpoons (AA-AN)^+$ (7)	
$(AA-AN)^+ + AA^+ \rightleftharpoons (AA-AN)^{2+} + AA$ (8)	
$(AA-AN)^{2+} \rightarrow DAA + 2H^+$ (9)	
	$-d[AA^+]/dt = k_{14}[AA^+]^2[AN]/(c_{14} + [AA])$ (14)
	$k_{14} = 2k_9K_7K_8; c_{14} = k_9/k_{-8}$
	$k_{14} = 0.26 M^{-1} s^{-1}; c_{14} = 2.4 \times 10^{-3} M$
B. Disproportionation	
$2AA^+ \rightleftharpoons AA^{2+} + AA$ (10)	
$AA^{2+} + AN \rightarrow DAA + 2H^+$ (11)	
	$-d[AA^+]/dt = k_{15}[AA^+]^2[AN]/(c_{15}[AN] + [AA])$ (15)
	$k_{15} = 2k_{11}K_{10}; c_{15} = k_{11}/k_{-10}$
	$k_{15} = 0.40 M^{-1} s^{-1}; c_{15} = 4.0 \times 10^{-2}$
C. Diamagnetic dimer	
$2AA^+ \rightleftharpoons AA-AA^{2+}$ (12)	
$AA-AA^{2+} + AN \rightarrow DAA + AA + 2H^+$ (13)	
	$-d[AA^+]/dt = k_{16}[AA^+]^2[AN]/(c_{16} + [AN])$ (16)
	$k_{16} = 2k_{12}; c_{16} = k_{-12}/k_{13}$

Kinetic data for the reaction of AA^+ with AN in CH_2Cl_2 -TFA-TFAn (97:2:1) are summarized in Table 2. The data in Table 2 have been corrected for the competing reaction, trifluoroacetoxylation of AA^+ .

Three sets of experiments, at three different $[AA]$ and varying $[AN]$, allow for a qualitative description of the mechanism of the pseudo second order reaction. At $[AA]$ equal to 8×10^{-4} M, a ten-fold

increase in $[AN]$ resulted in a 3.6-fold increase in k_{obs} (runs 1, 4, 5, 26; 28; 29, 30; 17; 31). A 5.7-fold enhancement in k_{obs} (runs 32-36) was observed for a 10-fold increase in $[AN]$ at $[AA]=26 \times 10^{-4}$ M. At a low $[AA]$, 2.2×10^{-4} M, and high $[AN]$ a 2-fold increase in $[AN]$ brought about a 1.6-fold change in k_{obs} (runs 37-39). The first two sets of experiments show a fractional order in $[AN]$ and implicate the disproportionation mechanism. How-

Table 2. Pseudo second order reaction between AA^+ and AN.^a

Run No.	$[AA] \times 10^4$	$[AA^+] \times 10^4$	$[AN] \times 10^2$	$k_{obs}/M^{-1} s^{-1}$	$k_{obs}^{disp}/M^{-1} s^{-1} b$	$k_{obs}^{comp}/M^{-1} s^{-1} c$
1	8.22	1.23	1.84	6.0	4.7	1.5
2	7.12	2.33	1.84	6.1	5.1	1.5
3	5.48	3.56	1.84	7.0	4.7	1.6
4	7.75	1.88	1.84	7.0	4.9	1.5
5	7.5	2.00	1.84	6.7	5.0	1.5
6	11.8	2.63	1.84	4.7	3.8	1.3
7	12.4	2.25	1.84	4.2	3.7	1.3
9	18.5	2.06	1.84	3.2	2.9	1.1
10	25.3	2.00	1.84	2.7	2.3	1.0
11	7.75	2.13	6.44	13.0	7.7	5.3
12	11.8	2.38	6.44	10.4	6.9	4.7
13	17.3	2.25	6.44	8.4	6.0	4.1
14	22.8	2.25	6.44	7.5	5.3	3.6
15	26.9	2.25	6.44	7.3	4.9	3.3
16	6.99	2.26	18.4	25.0	9.1	15.4
17	7.30	2-24	18.4	24.0	9.1	15.3
18	12.2	2.63	18.4	20.6	8.6	13.2
19	17.2	2-50	18.4	19.5	8.1	11.6
20	22.6	2.37	18.4	17.5	7.7	10.3
21	27.3	2.05	18.4	17.0	7.3	9.3
22	7.21	2.28	46	51	9.6	38.3
23	11.9	2.38	46	43	9.4	33.3
24	16.1	2.25	46	40	9.2	29.8
25	20.6	2.25	46	38	9.0	26.8
26	8.00	2.06	1.84	7.2	4.8	1.5
27	7.19	2.60	4.6	10.0	7.2	3.8
28	7.88	2.00	4.6	9.9	7.0	3.8
29	7.81	2.40	9.2	14.0	8.3	7.5
30	8.50	2.19	9.2	14.5	8.1	7.4
31	8.13	2.25	18.4	24.8	9.0	14.9
32	25.8	2.00	1.84	3.0	2.2	1.0
33	25.6	2.13	4.6	6.3	4.2	2.4
34	22.9	2.46	9.2	11.6	6.2	5.1
35	26.6	2.13	9.2	11.0	5.8	4.7
36	26.3	2.13	18.4	17.0	7.3	9.5
37	1.73	0.38	23	34	9.8	23.0
38	2.23	0.45	23	33	9.8	22.8
39	2.18	0.48	46	56	9.9	45.7

^a Solvent: CH_2Cl_2 -TFA-TFAn (97:2:1); supporting electrolyte, Bu_4NBF_4 (0.1 M); temp. 11 °C; concentrations in mol l^{-1} . ^b Calculated on the basis of $k_{obs}^{disp} = 0.4[AN]/(4.0 \times 10^{-2}[AN] + [AA])$. ^c Calculated on the basis of $k_{obs}^{comp} = 0.26[AN]/(2.4 \times 10^{-3} + [AA])$.

ever, the expected decreasing dependence on $[AN]$ as the latter was increased was not observed. The extreme case, where $[AA]$ was low and $[AN]$ was high gave roughly first order dependence while in the light of the other two series, k_{obs} was predicted to be independent of $[AN]$ under these conditions by rate law (15). Thus, the occurrence of two competing second order mechanisms was established.

Assuming that the disproportionation and complexation mechanisms are the competing reaction pathways giving the overall pseudo second order rate constants, k_{obs} , it is possible to evaluate the magnitude of the components of k_{obs} , i.e. k_{obs}^{disp} and k_{obs}^{comp} arising from disproportionation and complexation, respectively. Eqns. (17) and (18) give the relationships between the components of k_{obs} and k_{app} values which are normalized for $[AA]$ and $[AN]$. The constant a and k_{app}^{comp} were then evaluated

$$k_{obs}^{comp} = k_{app}^{comp}[AN]/(a + [AA]) \quad (17)$$

$$k_{obs}^{disp} = k_{app}^{disp}[AN]/(b[AN] + [AA]) \quad (18)$$

accomplished by an iterative procedure. As a starting point, it was assumed that at $[AN]$ equal to 1.84×10^{-2} and 4.6×10^{-2} M, complexation was not important and $k_{obs} = k_{obs}^{disp}$. This assumption allowed for the estimation of b and k_{app}^{disp} in eqn. (18). In order to evaluate a and k_{app}^{comp} in eqn. (17), k_{obs}^{disp} was calculated at $[AN] = 1.84 \times 10^{-2}$. Eqn. (19) was then used to evaluate k_{obs}^{comp} at that value of $[AN]$. The constant a and k_{app}^{comp} were then evaluated

$$k_{obs} = k_{obs}^{disp} + k_{obs}^{comp} \quad (19)$$

from the least squares correlation line of $1/k_{obs}^{comp}$ vs. $[AA]$ at $[AN] = 1.84 \times 10^{-2}$ M. Both k_{obs}^{comp} were then calculated for all runs summarized in Table 2 and the agreement with (19) checked. The sum of k_{obs}^{disp} and k_{obs}^{comp} was of the order 1.2 times as great as k_{obs} at $[AN] = 1.84 \times 10^{-2}$ M indicating that the original assumption that the disproportionation reaction predominates at the lowest values of $[AN]$ was not correct. Values of k_{obs}^{disp} at $[AN]$ of 1.84×10^{-2} M estimated from eqn. (19) and values of k_{obs}^{comp} calculated during the first iteration were then used to reevaluate k_{app}^{disp} and then a new a and k_{app}^{comp} were estimated as before. The values of k_{obs}^{disp} and k_{obs}^{comp} shown in Table 2 resulted from the third iteration. The least squares correlation line of k_{obs} vs. $k_{obs}^{disp} + k_{obs}^{comp}$ had a slope equal to 1.0 and an

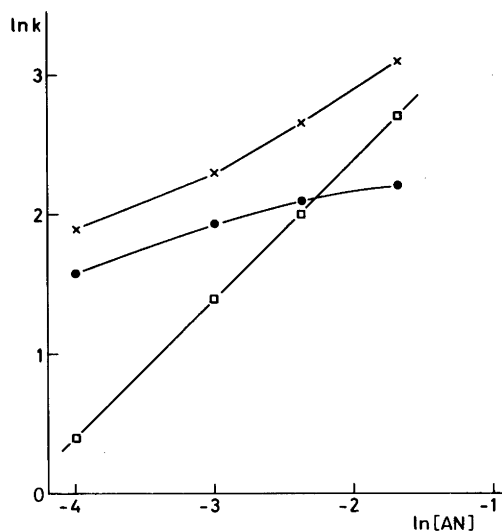


Fig. 1. Dependence of k_{obs} on $[AN]_0$ for the pseudo second order reaction between AA^+ and AN in CH_2Cl_2 -TFA-TFAn (97:2:1) at 11° ($[AA]_0 = 8 \times 10^{-4}$ mol/l). \times , Experimental points: \circ , $\ln k_{obs}^{disp}$; \square , $\ln k_{obs}^{comp}$.

intercept close to zero ($-0.5 \text{ M}^{-1} \text{ s}^{-1}$) in accordance with expectation from eqn. (19).

The dependence of k_{obs} , as well as the calculated rate constants k_{obs}^{comp} and k_{obs}^{disp} , on $[AN]$ at constant $[AA]$ is illustrated in Fig. 1. At low values of $[AN]$, the slope of the $\ln k_{obs}$ vs. $\ln [AN]$ line is very close to that of the $\ln k_{obs}^{disp}$ vs. $\ln [AN]$ line while at the other extreme of $[AN]$ it more closely corresponds to the $\ln k_{obs}^{comp}$ vs. $\ln [AN]$ slope. The latter is again a demonstration of the increasing importance of complexation relative to disproportionation with increasing anisole concentration.

It can be seen from eqns. (17) and (18) that both the complexation and disproportionation mechanisms predict a linear relationship when $1/k_{obs}^{comp}$ and $1/k_{obs}^{disp}$ are plotted vs. $[AA]$ at constant $[AN]$. Under conditions where a reaction follows only the complexation or the disproportionation mechanism, the intercept of the corresponding plot is related to a (eqn. 17) or $b[AN]$ (eqn. 18). Thus, the intercepts of the plots divided by $[AN]$ are proportional to $a/[AN]$ and b , respectively. That is, the disproportionation mechanism requires that the intercept be independent of $[AN]$ while the complexation mechanism predicts an intercept inversely proportional to $[AN]$. Plots of $1/k_{obs}$ vs. $[AA]$ were

Table 3. The effect of anisole concentration on the intercepts of plots of observed rate constants as a function of 9-anisylanthracene concentration.

[AN]/10 ⁻²	Intercept	Relative intercept	Comp. int. ^a	Dis. int. ^b
1.84	0.073	1.0	1.0	1.0
6.44	0.057	0.78	0.29	1.0
18.4	0.034	0.46	0.10	1.0
46.0	0.017	0.23	0.04	1.0

^a Relative intercept predicted according to eqn. (17) assuming only the complexation mechanism. ^b Relative intercept predicted according to eqn. (18) assuming only the disproportionation mechanism.

constructed at four different values of [AN]. The intercepts, relative intercepts and those predicted by the two mechanisms operating independently are summarized in Table 3. For the range of [AN] studied, the observed intercept changed by a factor of 4 while the disproportionation mechanism required a constant value of the intercept and the complexation mechanism predicted a change of 20 in going from the high to the low [AN].

DISCUSSION

The disappearance of the 9-anisylanthracene cation radical in solutions (solvent = CH₂Cl₂ - TFA - TFAN, 97:2:1) containing excess AA and anisole follows a second order rate law. In the absence of AN, the disappearance of AA⁺ still follows a second order rate law but with a much lower rate constant. The latter reaction leads to the

formation of 9-anisyl-10-trifluoroacetoxyanthracene. The reaction with anisole, leading to the formation of 9,10-dianisylanthracene, cannot be described by a single mechanism. The dependence of *k*_{obs} on both [AN] and [AA] shows that the reaction is complex, following at least two mechanisms.

Before going on with a discussion of the data, it is of interest to examine the criteria generally used in assigning mechanisms to similar reactions. The observation of kinetics second order in radical ion and inhibition by parent aromatic compound has been the major evidence used in the assigning of disproportionation mechanisms to radical ion reactions. A number of such reactions, for which kinetic data are available, are summarized in Table 4. In all of the reactions listed, the only kinetic evidence which was found in support of the disproportionation mechanism was that previously men-

Table 4. Reactions of radical ions for which disproportionation mechanisms have been proposed.

Reactants	Mechanistic evidence	Ref.
A. Thianthrene cation radical + water	Second order in radical ion, inhibition by parent aromatic.	2, 3
B. Thiathrene cation radical + anisole	Second order in radical ion, inhibition by parent aromatic.	4
C. Thianthrene cation radical + phenol	Second order in radical ion, inhibition by parent aromatic.	13
D. Tetraphenylethylene cation radical cyclization	Second order in radical ion. Direct measurement of the dication cyclization rate constant.	1a
E. Perylene ^{•-} + alcohols	Second order in radical ion, inhibition by parent aromatic. Feasibility tested by analysis of the disproportionation equilibrium constant.	
F. Anthracene ^{•-} + <i>t</i> -BuOH	Second order in radical ion, some inhibition by parent aromatic. Feasibility tested by analysis of the disproportionation equilibrium constant. An alternate mechanism, protonation of the dianion dimer ruled out from the dependence of the rate on [<i>t</i> -BuOH].	6, 14, 15

tioned, second order in radical ion and inhibition by parent aromatic. The reactions involving radical anions have been studied in more detail. Disproportionation equilibrium constants were calculated from potentiometric titration data and the feasibility of the mechanisms were discussed by estimation of pertinent rate constants.

Reactions A, B and C (Table 4) involving the thianthrene cation radical have been reinvestigated.¹ The dependence of the rates of the reactions upon nucleophile and unoxidized thianthrene concentrations clearly eliminate both the disproportionation and the diamagnetic dimer dication mechanisms (Table 1) from consideration. The data fit rate law (14) and thus the complexation mechanism has been assigned to these reactions.

It is clear that the observation of kinetics second order in radical ion is not sufficient evidence for assigning any of the mechanisms listed in Table 1. The diamagnetic dimer mechanism is easily tested for since rate law (16) requires that the reaction rate should be independent of the parent aromatic compound. Most of the second order reactions found to date are found to be inhibited by the presence of parent aromatic compound which suggests that the diamagnetic dimer mechanism is not commonly encountered. The complexation and disproportionation mechanisms are more difficult to distinguish. Under conditions of fast equilibria, rate laws (14) and (15) become identical. Therefore, in order to distinguish between the latter mechanisms, conditions must be found under which the two rate laws are different. The last three reactions in Table 4 were studied under conditions of fast equilibria and thus the data do not allow for definite mechanism assignments. The complexation mechanism cannot apply to reaction D, the cyclization of the tetraphenylethylene cation radical, since a second reactant is required for that mechanism. The direct rate measurements on the dication strongly support the disproportionation mechanism in the latter case.^{1a} Direct measurements of dianion protonation rates⁸ support the assignment of disproportionation mechanisms for reactions E and F. Further support for the disproportionation mechanism for reaction E, the protonation of perylene anion radical by alcohols, has been claimed on the basis of CIDNP experiments.¹⁶ The latter results do suggest that the anion radicals are not directly protonated but do not distinguish between any of the mechanisms in Table 1.

It is obvious from the previous discussion that in

order to distinguish between the complexation and disproportionation mechanisms it is necessary to conduct kinetic studies under conditions where the relevant equilibria are not fast compared to the product forming reactions. In terms of the general rate equation for the disproportionation mechanism (eqn. 4), the condition necessary is given by (20); i.e. the ratio of the rate constant for the product forming step (k_3) to that for back reaction of the disproportionation (k_{-2}) multiplied by the concentration of the second reactant must be equal or greater than one tenth the concentration of the parent aromatic compound. If we assume that k_{-2} is a diffusion controlled rate constant equal to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, eqn. (21) gives the ratio of parent aromatic to second reactant concentrations for a particular product forming rate constant which must be used in order that the reaction does not proceed under equilibrium conditions. For example, we can consider the conditions that it would be necessary to employ to avoid equilibrium for reaction E (Table 4) where the protonating agent is

$$k_3/k_{-2}[\text{R}] \geq 0.1[\pi] \quad (20)$$

$$k_3 \geq 10^9[\pi]/[\text{R}] \quad (21)$$

t-BuOH: The latter reaction has been studied thoroughly under equilibrium conditions and k_3 has been estimated to be of the order of $10^6 \text{ M}^{-1} \text{ s}^{-1}$.⁵ From (21) we see that it would be necessary operate with $[\pi]/[\text{R}] \leq 10^{-3}$ to avoid equilibrium conditions. The kinetic studies were conducted with $[\pi]/[\text{R}] \geq 2 \times 10^{-2}$. Thus, further kinetic studies in which the concentration ratio is reduced by a factor of 20 or more would be necessary in order to distinguish between the disproportionation and complexation mechanisms for that reaction.

The constants in rate laws (14) and (15) for the complexation and disproportionation mechanisms (Table 1) were estimated from the rate data in Table 2 along with eqns. (17) and (18). The pertinent rate and equilibrium constants for the two mechanisms may be estimated from the values of the constants.

Turning first to the complexation mechanism, we can evaluate the rate constant for the product forming reaction, k_9 , by assuming that k_{-8} is equal to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, the value for a diffusion controlled reaction. The latter is reasonable since electron transfer rates for energetically favorable reactions of aromatic ions with aromatic compounds have been found to be diffusion controlled.¹⁷

Thus, we estimate k_9 to be equal to $2.4 \times 10^7 \text{ s}^{-1}$. Likewise, the equilibrium constant product, $K_7 K_8$, is estimated to be equal to $5.4 \times 10^{-9} \text{ M}^{-1}$.

If we assume that k_{-10} of the disproportionation equilibrium is equal to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, k_{11} is estimated to be equal to $4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The latter leads to a value of 5.0×10^{-10} for the disproportionation equilibrium constant, K_{10} . The difference in E° values for formation of AA^+ and AA^{2+} is then estimated to be equal to 549 mV under the conditions used in this study. The measured value, 410 mV at 100 mV/s, is smaller than the reversible value due to the reaction of AA^{2+} with TFA. The pseudo first order rate constant for the latter reaction can then be estimated from the difference in reversible and irreversible peak potentials using the formula given by Nicholson and Shain.¹⁸ The value estimated is $3.2 \times 10^5 \text{ s}^{-1}$.

It is of interest to compare equilibria (8) and (10). Both involve the oxidation of a cation by AA^+ . The equilibrium constant for (10) was estimated to be equal to 5.0×10^{-10} while the product $K_7 K_8$ was evaluated to be $5.4 \times 10^{-9} \text{ s}^{-1}$. Since we have not been able to detect $(\text{AA}-\text{AN})^+$ in this study or similar complexes in others,¹ we can set the maximum value of K_7 at 10 M^{-1} which under the conditions of this study would correspond to a concentration ratio $[(\text{AA}-\text{AN})^+]/[\text{AA}^+]$ equal to 10^{-2} . If K_7 is estimated at 10 M^{-1} , K_8 is then equal to 5.4×10^{-10} , i.e. nearly identical to the value estimated for K_{10} . It seems more reasonable that K_8 would be considerably greater than K_{10} since the polarization of the electron rich anisole moiety in the complex $(\text{AA}-\text{AN})^+$ would be expected to substantially lower the oxidation potential of the AA^+ moiety. Thus, a prediction of 120 mV difference in the oxidation potentials of AA^+ and $(\text{AA}-\text{AN})^+$ leads to an estimate of K_8/K_{10} equal to 10^2 which in turn gives a value of 10^{-1} to K_7 and 5.4×10^{-8} to K_8 . The latter values give a clear reason for the failure to detect the complex since $[(\text{AA}-\text{AN})^+]/[\text{AA}^+]$ is predicted to be of order of 10^{-4} leading to a value of the order of 10^{-8} M for the concentration of the complex.

To definitively establish mechanisms of reaction from kinetic data when two or more competing reactions are involved is an exceedingly difficult task. The data presented here serve as a strong indication that complexation and disproportionation mechanisms can compete during the reactions of a cation radical. It is also apparent that other

reactions which have been assigned the disproportionation mechanism may in fact proceed partially or totally by the complexation mechanism. In all cases, further work is necessary in order to differentiate between the two mechanisms.

EXPERIMENTAL

Dichloromethane was passed through a column of neutral alumina (Woelm W 200) immediately before use. Trifluoroacetic acid and trifluoroacetic acid anhydride were used as obtained (Fluka, purum grade).

The apparatus used for voltammetric measurements¹⁹ and the cell^{1b,d,e} used both for the kinetic study and for the preparation of the cation radical solutions have been described. The procedure used for carrying out the kinetic runs was that previously described.^{12,1e}

Preparation of DAA from AA. 9-Anisylantracene (10 mmol) in CH_2Cl_2 -TFA-TFAn (97:2:1) containing Bu_4NBF_4 (0.2 M) and anisole (100 mmol) were subjected to anodic oxidation at a platinum gauze electrode at a constant current of 200 mA in the cell previously described.^{1b,d,e} After 3 F mol^{-1} had passed, the product cation radical was reduced by adding Zn to the anolyte. After stirring for 2 h, the solution was filtered and evaporated almost to dryness. A small amount of MeCN was added to the residue and the product precipitated upon cooling (90% yield). The product was recrystallized in MeCN- CH_2Cl_2 and was identical with authentic 9,10-dianisylantracene.

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