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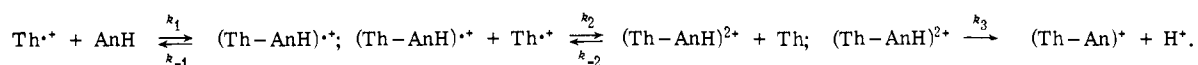(28) F. E. Ray and G. Rieveschl, Jr., "Organic Syntheses," Collect. Vol. III,

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Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. II.[1] Anisylation of Thianthrene Cation Radical

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Abstract: The thianthrene cation radical ($Th \cdot^+$) reacts with anisole (AnH) to give a complex which reacts further by one of two pathways depending upon the concentration of the cation radical. At low cation radical concentration ($\sim 10^{-5}$ M), a pseudo-first-order rate law is followed. Electrochemical techniques indicate that the reduction of $Th \cdot^+$ to thianthrene (Th) is a quantitative reaction under these conditions. At higher cation radical concentration the reaction becomes more complex obeying the rate law $-d[Th \cdot^+]/dt = 2k_3K_1K_2[Th \cdot^+]^2[AnH]/(k_3/k_{-2} + [Th])$, where the K's and k's are equilibrium constants and rate constants for the following equations. Dibenzo-p-dioxin cation radical ($DBO \cdot^+$) was found to accelerate

$$Th \cdot^+ + AnH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Th-AnH) \cdot^+; \quad (Th-AnH) \cdot^+ + Th \cdot^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (Th-AnH)^{2+} + Th; \quad (Th-AnH)^{2+} \overset{k_3}{\longrightarrow} (Th-An)^+ + H^+.$$

the rate of anisylation of $Th \cdot^+$ by a factor of 200 which was attributed to $DBO \cdot^+$, a better oxidant than $Th \cdot^+$, participating in equilibrium 2. A disproportionation mechanism was ruled out, because the observed rate constants were found to be as much as 5×10^4 times higher than predicted for diffusion-controlled reaction of Th^{2+}.

During the past few years, the mechanisms of the reactions of aromatic cation radicals have been under vigorous discussion in the literature. At about the same time, two different mechanisms for electrophilic reactions of cation radicals were published. Shine and Murata[2,3] proposed that the hydroxylation of the thianthrene cation radical ($Th \cdot^+$) involved a disproportionation to the reactive dication, while Manning, Parker, and Adams[4] proposed that the pyridination of the 9,10-diphenylanthracene cation radical involved a direct electrophilic reaction of the radical ion. A cross refutation of the two mechanisms appeared shortly afterward: Parker and Eberson[5] presented evidence that the hydroxylation of $Th \cdot^+$ involved a direct electrophilic reaction of the radical ion, while Marcoux[6] proposed that the pyridination of the 9,10-diphenylanthracene cation radical followed the disproportionation mechanism. More recently, the observation of reversible cation radical-dication redox couples in acetonitrile has given a reliable equilibrium constant for the disproportionation of $Th \cdot^+$ and has indicated that disproportionation reactions are very unlikely for the radical ion.[7] Furthermore, a homogeneous kinetic study of the pyridination of the 9,10-diphenylanthracene cation radical has confirmed that the radical ion reacts directly with pyridine.[8]

The initial reaction of a cation radical with a nucleophile produces a radical more easily oxidized than the substrate from which the radical ion is derived. A further one-electron oxidation of the radical is necessary to obtain stable products. When the reaction takes place at an electrode, electron transfer to the electrode can take place. However, in homogeneous solution the oxidant is usually a second equivalent of cation radical which is thereby reduced to substrate. This reaction has been called the half-regenera-

tion mechanism and has been demonstrated in several cases.[9] However, it should be pointed out that this terminology only describes the stoichiometry of the reaction and says little about the mechanism since it does not define the reactive species, *i.e.*, cation radical, dication, etc.

Recently, Silber and Shine[10] have reported the reaction of $Th \cdot^+$ with anisole (AnH) to give a sulfonium salt (eq 1).

$$(1)$$
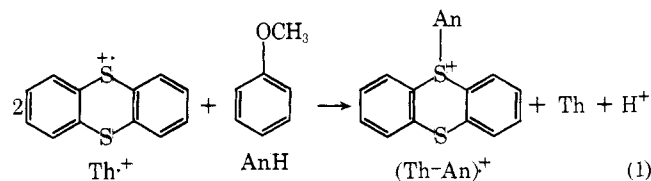
The reaction was found to be second order in cation radical and inhibited by unoxidized substrate, conditions expected for the disproportionation mechanism. Since the more recent work has cast serious doubt on disproportionation mechanisms for $Th \cdot^+$,[7] the anisylation reaction was reinvestigated in order to establish the mechanism.

Results

Voltammetric Anisylation of the Thianthrene Dication. In "nucleophile-free" acetonitrile,[7] the reversible first and second charge transfers from Th appear at +1.26 and +1.77 V.[11] In the same medium, AnH is oxidized irreversibly with a peak potential of +1.71 V. The cyclic voltammogram of Th (1.0 mM) in acetonitrile containing n-Bu$_4$NBF$_4$ (0.2 M) over neutral alumina is shown in Figure 1a which shows the two reversible couples. The addition of AnH (0.2 mM) had no effect upon the first charge transfer, but a pre-peak
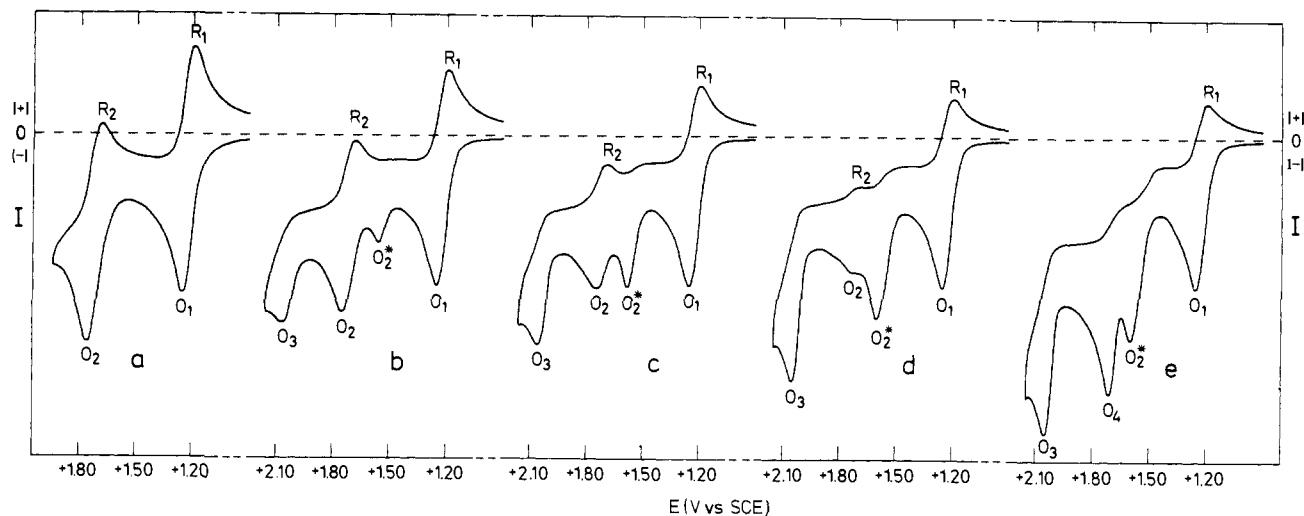
Figure 1. Cyclic voltammograms for the oxidation of Th (1.0 mM) in acetonitrile containing n-Bu$_4$NBF$_4$ (0.2 M) in the presence of neutral alumina and anisole, [AnH] = 0 (a), 0.2 mM (b), 0.4 mM (c), 0.6 mM (d), and 1.0 mM (e). Voltage sweep rate = 86 mV/sec.
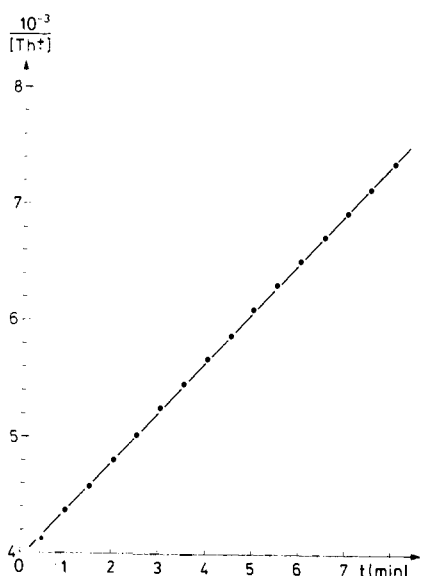
peak appeared at about 190 mV cathodic of the cation radical oxidation peak.

Kinetics of the Anisylation of the Thianthrene Cation Radical in Dichloromethane–Trifluoroacetic Acid–TFA Anhydride. A number of runs were conducted in CH$_2$Cl$_2$–TFA (49:1). However, Th·$^+$ was not stable in this medium, and the kinetics of the anisylation reaction were complicated by competing reactions. The latter problem was completely overcome by the inclusion of TFAn (1%) in the solvent system. In the presence of excess AnH, clean pseudo-second-order kinetics were observed for the anisylation of Th·$^+$ in CH$_2$Cl$_2$–TFA–THAn (97:2:1) as illustrated by the plot of $1/$[Th·$^+$] vs. time in Figure 2. Several runs were conducted in CH$_2$Cl$_2$–TFA–TFAn (97:2:1) containing n-Bu$_4$NBF$_4$ (0.1 M) in which the dependence of the observed rate constant (k_{obsd}) on the unoxidized Th and the AnH concentrations was determined. These runs are summarized in Table I. At a constant value of [AnH], the observed second-order

Figure 2. Second-order rate plot for the anisylation of Th·$^+$ in dichloromethane–TFA–TFAn (97:2:1) containing n-Bu$_4$NBF$_4$ (0.1 M) and AnH (1.84 × 10^{-2} M). Temp, 13°.

was observed at +1.58 V (Figure 1b). Further addition of AnH (0.4 mM) resulted in an increase in the height of the pre-peak at the expense of the peak due to oxidation of Th·$^+$ (Figure 1c). When the concentration of AnH was 0.6 mM,[12] the Th·$^+$–Th^{2+} couple was barely visible (Figure 1d). Addition of more AnH (1.0 mM) did not change the pre-peak, but a peak for the oxidation of AnH appeared (Figure 1e). The Th–Th·$^+$ couple remained completely reversible upon further addition of AnH until about a concentration of 32 mM where a slight decrease in $i_{\text{pc}}/i_{\text{pa}}$ was observed. Some reversibility of the latter couple was still evident when the AnH concentration was increased to 250 mM.

In a mixed solvent consisting of dichloromethane–trifluoroacetic acid (TFA)–trifluoroacetic acid anhydride (TFAn) (45:5:5), the peak separation for the two charge transfers from Th is equal to 640 mV. No change can be observed in the Th–Th·$^+$ couple even at very high AnH concentrations. The same behavior as in acetonitrile was observed in the region of the second charge transfer; a pre-peak proportional to the amount of AnH added was observed at anisole concentrations less than 1.0 mM. The pre-

Table I. Anisylation of the Thianthrene Cation Radical in Dichloromethane. Dependence of k_{obsd} on the Concentration of Thianthrene and Anisole[a]

Run no.	[Th]$_0$ × 10^4	[Th·$^+$]$_0$ × 10^4	[AnH] × 10^2	k_{obsd}, M^{-1} sec^{-1}	k_{app}, M^{-1} sec^{-1}
15	1.35	8.64	1.84	2.08	0.155
13	4.20	5.80	1.84	1.62	0.146
14	7.20	2.80	1.84	1.48	0.157
18	8.60	1.40	1.84	1.01	0.115
16	13.40	6.20	1.84	0.80	0.112
20	28.10	6.90	1.84	0.59	0.130
19	54.70	5.30	1.84	0.38	0.139
				Av	0.136 ± 0.023
21	6.74	3.05	0.92	0.69	0.143
22	6.69	3.21	3.69	2.73	0.141
23	6.63	3.21	7.37	5.96	0.147
53	0.25	1.23	46.0	1600	4.4[b]

[a] Solvent composition: CH$_2$Cl$_2$–TFA–TFAn (97:2:1); [n-Bu$_4$-NBF$_4$] = 0.1 M; temp 13°. All concentrations in mol/l. k_{obsd} = k_{app}[AnH] M^{-1} sec^{-1})/(1.24 × 10^{-3} + [Th]). [b] This run, which was included to demonstrate the very large k_{obsd}, was on the borderline of the measurement technique, and k_{app} is therefore in doubt.

rate constant (k_{obsd}) was found to decrease with increasing [TH]$_0$. A linear relationship was found by plotting $1/k_{\text{obsd}}$ vs. [Th]$_0$, and a slope of 404 sec and an intercept of 0.50 M sec were obtained. From the latter, it is readily shown that the following relationship (eq 2) holds for a particular value
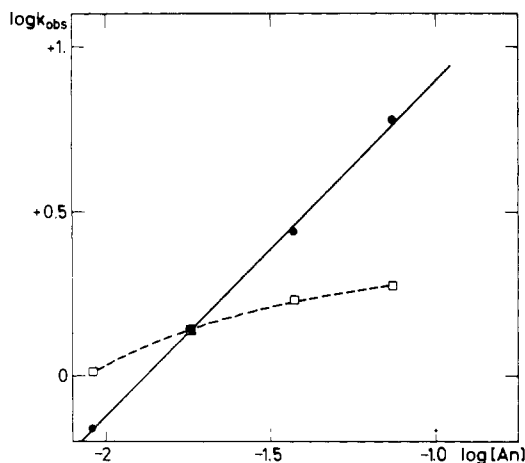
Figure 3. Dependence of k_{obsd} on [AnH] for the anisylation of Th·+ in dichloromethane-TFA-TFAn (97:2:1) at +13°. Circles are the observed data, and squares give the calculated points according to the disproportionation mechanism.

$1/k_{obsd} = (404[Th]_0 + 0.50)M$ sec or

$$k_{obsd} = \frac{2.47 \times 10^{-3} \, M^{-1} \, \text{sec}^{-1}}{1.24 \times 10^{-3} + [Th]_0} \quad (2)$$

of [AnH], *i.e.*, 1.84×10^{-2} M. The dependency of the rate on [AnH] was found from k_{app} which is normalized both for $[Th]_0$ and [AnH]. Thus, the constant value of k_{app}

$$k_{obsd} = k_{app}\frac{[AnH] \, M^{-1} \, \text{sec}^{-1}}{1.24 \times 10^{-3} + [Th]_0} \quad (3)$$

when [AnH] was varied by a factor of about 10 shows that the rate is directly proportional to the anisole concentration. The validity of the relationship is further shown by Figure 3.

Kinetics of the Anisylation of the Thianthrene Cation Radical in Acetonitrile-TFAn. The background reaction of Th·+ with water was very difficult to control, and the rate constants for the anisylation reaction were not reproducible. As in the dichloromethane case, the difficulty was overcome by including the very effective water scavenger, TFAn (1%). The same treatment as described in the preceding section was used to evaluate the dependency of the rate of the reaction on $[Th]_0$ and [AnH]. The data are summarized in Table II, and the equations for k_{obsd} and k_{app} derived from a plot of $1/k_{obsd}$ vs. $[Th]_0$ are given in eq 4 and 5.

$$k_{obsd} = \frac{0.410 \, M^{-1} \, \text{sec}^{-1}}{2.13 \times 10^{-3} + [Th]_0} \quad (4)$$

$$k_{obsd} = k_{app}\frac{[AnH] \, M^{-1} \, \text{sec}^{-1}}{2.13 \times 10^{-3} + [Th]_0} \quad (5)$$

Several runs were conducted to test for possible salt effects and temperature dependence for the anisylation of Th·+ in acetonitrile. The data are tabulated in Table III. It is seen that a very small positive kinetic salt effect is observed upon increasing the salt concentration from 0.1 to 0.4 M (runs 47, 40, 39, and 41). In order to ensure that the inclusion of small amounts of TFAn in the solvent system did not alter the reaction, the concentration was changed by a factor of 5 (runs 47, 42, and 43). The results were virtually identical for the three runs. Only about a 20% increase in k_{obsd} was found when the temperature was increased from 12 to 20° (runs 47 and 44).

First-Order Rate Constants for the Reaction of Th·+ at Low Cation Radical Concentrations. Runs conducted at

Table II. Anisylation of the Thianthrene Cation Radical in Acetonitrile. Dependence of k_{obsd} on the Concentration of Thianthrene[a]

Run no.	$[Th]_0 \times 10^4$	$[Th\cdot^+]_0 \times 10^4$ Total	Monomer[d]	k_{obsd}, $M^{-1} \text{ sec}^{-1}$	k_{app}, $M^{-1} \text{ sec}^{-1}$
28	4.40	5.49	3.00	165	46.3
27	7.00	3.00	1.96	141	43.6
24	15.80	4.15	2.46	108	43.8
25	30.80	4.15	2.46	76.8	43.5
26	50.80	5.12	2.86	56.7	44.4
				Av	44.3 ± 1.4
54[b]	6.95	3.12	2.00	195	59.9
55[b,c]	0.31	1.22	0.92	21,500	101

[a] Solvent composition: MeCN-TFAn (99:1), $[n\text{-Bu}_4\text{NBF}_4]$ = 0.1 M; [AnH] = 9.2×10^{-3} M. Concentrations in mol/l.; temp 12°. $k_{obsd} = k_{app}$ $([AnH] \, M^{-1} \, \text{sec}^{-1})/(2.13 \times 10^{-3} + [Th]_0)$. [b] Contained $[NaClO_4]$ = 0.1 M as supporting electrolyte. [c] [AnH] = 460×10^{-3} M. [d] Concentration and rate constant corrected for equilibrium 11.

Table III. The Effect of Salt and TFAn Concentrations on the Rate of Anisylation of the Thianthrene Cation Radical[a]

Run no.	$[Th]_0 \times 10^4$	$[Th\cdot^+]_0 \times 10^4$	$[TFAn]^b$	$[n\text{-Bu}_4\text{NBF}_4]$	k_{obsd}, $M^{-1} \text{ sec}^{-1}$
(47)			1	0.1	87.7[c]
40	6.11	3.53	1	0.2	95.1
39	6.11	3.66	1	0.2	100
41	5.76	3.59	1	0.4	123
42	6.30	3.70	2	0.1	88.6
43	6.43	3.60	5	0.1	89.4
44	6.76	3.20	1	0.1	107.4[d]

[a] Solvent composition: MeCN-TFAn (99:1); [AnH] = 9.2×10^{-3} M; temp 12°. Concentrations in mol/l. [b] In ml/100 ml of solvent. [c] Value extrapolated from Figure 3. [d] Temp 24°.

$[Th\cdot^+]_0$ slightly less than 10^{-4} M gave very bad second- and first-order plots in either dichloromethane or in acetonitrile. However, when $[Th\cdot^+]_0$ was lowered further to close to 10^{-5} M, the data fit first-order plots very well. In runs where pseudo-second-order kinetics were observed, rotating disk electrode voltammetry showed that for every 2 mol of cation radical reacting 1 mol of thianthrene was generated. However, under conditions where pseudo-first-order kinetics were followed, 1 mol of thianthrene was produced for each 1 mol of cation radical reacting. Data for the anisylation of Th··+ at low concentration in both solvent systems are summarized in Table IV. Runs 35, 36, 37, and 38 show that the reaction is first order in anisole under these conditions also.

Anisylation of Thianthrene Cation Radical in the Pres-

Table IV. Pseudo-First-Order Reaction of the Thianthrene Cation Radical[a]

Run no.	$[Th]_0 \times 10^4$	$[Th\cdot^+]_0 \times 10^5$	[AnH] $\times 10^2$	$k_{obsd} \times 10^3$, $M^{-1} \text{ sec}^{-1}$
31	3.25	1.63	0.92	1.87
32	2.75	0.71	0.92	1.33
33	2.85	1.33	0.92	1.76
34	3.45	0.70	0.92	1.28
35	5	1.66	0.92	1.48
			Av	1.54 ± 0.3
36	2.55	0.64	0.092	0.276
37	3.45	1.14	1.84	3.56
38	2.46	1.0	3.68	6.64
45	2.66	0.92	9.2	0.219
46	3.42	3.04	9.2	0.255

[a] Solvent composition: runs 31-38, MeCN-TFAn (99:1), $[n\text{-Bu}_4\text{NBF}_4]$ = 0.1 M; runs 45-46, CH_2Cl_2-TFA-TFAn (97:2:1), $[n\text{-Bu}_4\text{NBF}_4]$ = 0.1 M; temp 12°. Concentrations in mol/l.

Table V. Anisylation of Thianthrene Cation Radical in the Presence of Dibenzo-p-dioxin Cation Radical[a]

Run no.	[DBO] $\times 10^4$	([Th$\cdot^+$]$_0$ + [DBO$\cdot^+$]$_0$) $\times 10^4$	[AnH] $\times 10^2$	k_{obsd} $\times 10^{4 b}$	k_{app} $\times 10^{3 b}$
48	7.52	4.0	9.2	2.66	7.72
49	6.72	4.10	9.2	1.7	4.79
50	7.81	3.10	0.92	0.182	5.34
51	7.81	3.10	0.92	0.164	4.81
52	9.60	5.60	0.92	0.249	7.79

[a] Temp, 11.5°, solvent MeCN-TFAn (99:1), [NaClO$_4$] = 0.1 M. Concentrations in mol/l. [b] In M^{-1} sec^{-1}.

ence of Dibenzo-p-dioxin Cation Radical (DBO$\cdot^+$). Several kinetic runs were conducted on the anisylation of Th$\cdot^+$ in MeCN-TFAn (99:1) in which the initial [Th$\cdot^+$] was accompanied by an equal [DBO$\cdot^+$]. These runs are summarized in Table V.

Equilibrium Constant for the Dimerization of the Thianthrene Cation Radical in Acetonitrile at 11.7 ± 0.2°. The thianthrene cation radical exists in solution in dynamic equilibrium with a diamagnetic dimer.[13,14] This equilibrium appeared to be of greater importance in acetonitrile than in dichloromethane in preliminary experiments, and thus it was necessary to assess the importance of the dimer-monomer equilibrium upon the kinetic results. The results in acetonitrile under the same conditions as used in the kinetic experiments are summarized in Table VI. The equilibrium constants were calculated from the visible absorption spectra at various total concentrations of oxidized Th. The monomer showed a single absorption maximum at 546 nm, while the dimer had maxima at 475 and 600 nm. The last three rows in Table VI give the calculated concentrations

Table VI. The Thianthrene Cation Radical Monomer-Dimer Equilibrium in Acetonitrile at 11.7 ± 0.2°

C_T,[a] $M \times 10^3$	C_D,[b] $M \times 10^4$	C_M,[c] $M \times 10^4$	K,[d] $M^{-1} \times 10^{-3}$
1.11	3.28	4.53	1.62
0.72	1.75	3.71	1.27
0.44	0.942	2.52	1.48
0.26	0.455	1.77	1.45
0.10	0.0953	0.809	1.46[e]
0.05	0.0285	0.443	1.46[e]
0.01	0.00138	0.0972	1.46[e]

[a] Total concentration of oxidized Th in the presence of excess Th (10^{-2} M) and sodium perchlorate (0.1 M). [b] Dimer concentration calculated from the absorption spectra. [c] Monomer concentration calculated from the absorption spectra. [d] Equilibrium constant for association of the cation radical. [e] Average value from the first four entries.
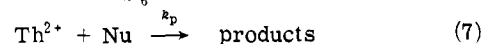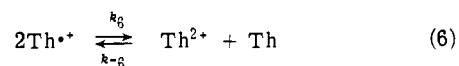
for monomer and dimer using the value for the equilibrium constant (1.46 × 10^3 M^{-1}) calculated from the experiments (lines 1-4, Table VI). It is evident from the data that at a total concentration of 10^{-4} M, 81% of oxidized species is in the monomeric form, while at 10^{-5} M, 97% of oxidized species are monomeric.

Product of the Reaction between Th$\cdot^+$ and AnH. Anodic oxidation of Th (10 mmol) in the presence of AnH (50 mmol) at constant current passed for 2.0 faradays/mol of Th in acetonitrile-TFAn (99:1) containing NaClO$_4$ resulted in the formation of (Th-An)$^+$ClO$_4^-$ which was isolated in 87% yield.[15] The salt, (Th-An)$^+$ClO$_4^-$, showed a single irreversible oxidation peak in acetonitrile at +2.06 V which matches the potential of O$_3$ in Figures 1b-e. Thus it was possible to identify the product voltammetrically under the conditions that the kinetic experiments were carried out in both acetonitrile-TFAn (99:1) and in dichloromethane-

TFA-TFAn (97:2:1). In either solvent, reaction of Th$\cdot^+$ (1.0 mM) with AnH (1.0 mM) appears to be quantitative judged from the peak height (O$_3$) due to the oxidation of (Th-An)$^+$ after reaction.

Discussion

The mechanisms of several reactions of aromatic cation radicals have been under discussion for several years now. Evidence allowing definitive assignment of mechanisms has been rather slow in surfacing. The reason for the latter is that mechanistic studies involving these reactive species can be exceedingly difficult. It has only been very recently that stable solutions of the cation radicals can be prepared in solvents other than strong acids which are not suitable for the study of reactions with nucleophiles, the reactions which are of the most current interest. Another difficulty is that electroanalytical techniques often fail to provide definitive evidence for the assignment of mechanisms when they are studied as electron transfer follow-up reactions. This is because some of the reactions appear to be much too complex to gain mechanistic information by the fitting of experimental data to theoretical working curves, a procedure which is not always reliable even for rather simple reactions.

$$2\text{Th}\cdot^+ \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \text{Th}^{2+} + \text{Th} \tag{6}$$

$$\text{Th}^{2+} + \text{Nu} \overset{k_p}{\longrightarrow} \text{products} \tag{7}$$

The disproportionation mechanism (eq 6 and 7) for reactions of Th$\cdot^+$ has been proposed[2,3,10] and has stimulated further studies.[5-8] Brief kinetic data have been presented to support the mechanism, and the reaction was proposed to follow the rate law (eq 8):[2,3,10]

$$d[\text{Th}\cdot^+]/dt = k_p K_{disp}[\text{Th}\cdot^+]^2[\text{Nu}]/[\text{Th}] \tag{8}$$

However, the data presented are not sufficient to state, for example, that the reactions are first order in nucleophile and negative first order in unoxidized Th. A disproportionation reaction which rigorously follows a rate law similar to eq 8 has recently been investigated. The anodic cyclization of tetraphenylethylene[16] has been shown to take place by an initial disproportionation followed by rate determining cyclization of the dication.[17] In the latter case, the rate was found to be inversely proportional to the concentration of unoxidized substrate, and the rate constants calculated from the homogeneous reactions of the cation radical were in close agreement with those obtained by rotating disk electrode voltammetry for the cyclization of the dication. Thus, this system can serve as a model for other possible disproportionation mechanisms.

In the case of the anisylation of the thianthrene cation radical, the voltammetric results show that the reaction is not very fast since reversibility of the Th-Th$\cdot^+$ couple was observed even when the anisole concentration in acetonitrile was as high as 250 mM. However, the reaction between Th^{2+} and An is very fast as shown by the appearance of a pre-peak at the second oxidation stage on the Th voltammograms in both acetonitrile (Figure 1) and in the mixed solvent. The difference in potential between that for oxidation of Th$\cdot^+$ and the pre-peak is 190 mV at a voltage sweep rate of 86 mV/sec. The rate constant for the reaction between the dication and anisole may be estimated from the pre-peak data to be of the order of 10^7 M^{-1} sec^{-1}.[18]
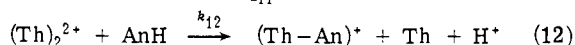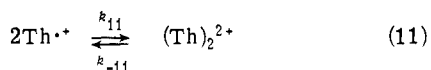
The observed dependency of k_{obsd} on [Th] found in this study does not fit eq 8. On the other hand, the dependency on both [Th$\cdot^+$] and [AnH] observed by Silber and Shine was confirmed. Thus inclusion of the proper [Th] dependency in the rate equation (eq 3 for the dichloromethane case and eq 5 for the acetonitrile case) results in eq 9 which is not

$$-\mathrm{d}[\mathrm{Th}^{\cdot+}]/\mathrm{d}t = k_{\mathrm{app}}[\mathrm{Th}^{\cdot+}]^2[\mathrm{AnH}]/(\text{constant} + [\mathrm{Th}]) \tag{9}$$

$$-\mathrm{d}[\mathrm{Th}^{\cdot+}]/\mathrm{d}t = k_{\mathrm{app}}[\mathrm{Th}^{\cdot+}]^2[\mathrm{AnH}]/([\mathrm{AnH}]\text{constant} + [\mathrm{Th}]) \tag{10}$$
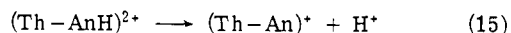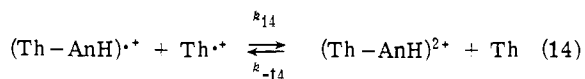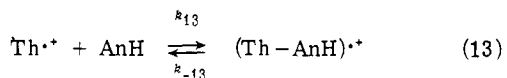
consistent with the disproportionation mechanism.[21] The disproportionation mechanism predicts that the reaction will be first order in [AnH] only if $k_{-6} \gg k_p$ which further requires that the plot of $1/k_{\mathrm{obsd}}$ vs. $[\mathrm{Th}]_0$ gives an intercept equal to zero. However, the intercepts observed for both solvent systems were substantially greater than zero. The observed [AnH] dependence is compared with that predicted by the disproportionation mechanism for the data in MeCN-TFAn in Figure 3. While the observed order in [AnH] is one, a significant deviation from a slope equal to one is predicted by the disproportionation mechanism. The latter mechanism can also be ruled out on other grounds. The equilibrium constant (K_{disp}) was calculated from voltammetric data[22] in both solvent systems and found to be equal to 3.2×10^{-11} in $\mathrm{CH_2Cl_2}$-TFAn and 1.1×10^{-9} in MeCN-TFAn. By use of the analysis previously presented,[23] the maximum possible values of k_{obsd} according to the disproportionation mechanism when k_p is rate determining were calculated to be $3.2 \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$ in the former and $1.6\ M^{-1}\ \mathrm{sec}^{-1}$ in the latter solvent systems. Values as high as 1.6×10^3 and $2.2 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ were observed in the two solvents, respectively. These values are between 5×10^4 and 10^4 times too great to be consistent with the disproportionation mechanism. Furthermore, the observed rate constants could no doubt be increased by another factor of 10^2 by suitable adjustment of $[\mathrm{AnH}]/[\mathrm{Th}]_0$. Thus, in our opinion, the disproportionation mechanism can be ruled out.

The observation that $\mathrm{Th}^{\cdot+}$ readily forms a dimeric species[13,14] suggested the dimer dication as a logical reactant (eq 11 and 12). While the latter mechanism satisfies

$$2\mathrm{Th}^{\cdot+} \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} (\mathrm{Th})_2^{2+} \tag{11}$$

$$(\mathrm{Th})_2^{2+} + \mathrm{AnH} \overset{k_{12}}{\longrightarrow} (\mathrm{Th}-\mathrm{An})^+ + \mathrm{Th} + \mathrm{H}^+ \tag{12}$$

the conditions of second order in cation radical, it does not predict inhibition by Th. There does not appear to be grounds for further discussion of this mechanism.

A mechanism which fits the kinetics (eq 9) involves initial complexation of $\mathrm{Th}^{\cdot+}$ with AnH (eq 13) to produce a species more easily oxidized than $\mathrm{Th}^{\cdot+}$, and electron transfer (eq 14) produces a thianthrene dication–anisole complex $(\mathrm{Th}-\mathrm{AnH})^{2+}$ which undergoes rate-determining bond formation with expulsion of a proton (eq 15) to produce the product, $(\mathrm{Th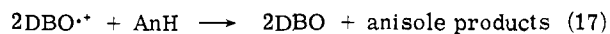}-\mathrm{An})^+$.[24] The steady-state approximation applied to $(\mathrm{Th}-\mathrm{AnH})^{2+}$ results in a rate eq 16 which with

$$\mathrm{Th}^{\cdot+} + \mathrm{AnH} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} (\mathrm{Th}-\mathrm{AnH})^{\cdot+} \tag{13}$$

$$(\mathrm{Th}-\mathrm{AnH})^{\cdot+} + \mathrm{Th}^{\cdot+} \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} (\mathrm{Th}-\mathrm{AnH})^{2+} + \mathrm{Th} \tag{14}$$

$$(\mathrm{Th}-\mathrm{AnH})^{2+} \longrightarrow (\mathrm{Th}-\mathrm{An})^+ + \mathrm{H}^+ \tag{15}$$

plied to $(\mathrm{Th}-\mathrm{AnH})^{2+}$ results in a rate eq 16 which with suitable substitution for k_{app}, and the Th term is identical with eq 9.[25] It was not possible to detect the proposed intermediate complex between $\mathrm{Th}^{\cdot+}$ and anisole, probably because of a small equilibrium constant for eq 10 in the tem-

$$-\mathrm{d}[\mathrm{Th}^{\cdot+}]/\mathrm{d}t = 2k_{15}K_{13}K_{14}[\mathrm{Th}^{\cdot+}]^2[\mathrm{AnH}]/(k_{15}/k_{-14} + [\mathrm{Th}]) \tag{16}$$

perature range where the rate measurements were made. At lower temperatures, dimerization of $\mathrm{Th}^{\cdot+}$[13,14] accounts for the principal species present in either of the solvents used. However, the association of radical ions with parent molecules is a well-documented phenomenon,[26] and the nucleophilicity of anisole would certainly be expected to be great enough to promote association with $\mathrm{Th}^{\cdot+}$.

Our recent observation that $\mathrm{DBO}^{\cdot+}$ undergoes an electron transfer reaction with anisole[27] with a k_{app} for reaction 17 being only 0.1 as great as that for $\mathrm{Th}^{\cdot+}$ with AnH,[28] suggested a test of the proposed mechanism (eq 13-15).

$$2\mathrm{DBO}^{\cdot+} + \mathrm{AnH} \longrightarrow 2\mathrm{DBO} + \text{anisole products} \tag{17}$$

$\mathrm{DBO}^{\cdot+}$ does not form a dimer detectable by visible absorption spectral measurements at temperatures as low as $-45°$ in MeCN and $-60°$ in dichloromethane. Thus, equilibrium 13 should lie further to the right than a comparable equilibrium involving $\mathrm{DBO}^{\cdot+}$. On the other hand, voltammetric data indicate that $\mathrm{DBO}^{\cdot+}$ has a reduction potential about 180 mV more positive than $\mathrm{Th}^{\cdot+}$, and thus K_{18} would be expected to be of the order of 10^3 times greater than K_{14}.

$$(\mathrm{Th}-\mathrm{AnH})^{\cdot+} + \mathrm{DBO}^{\cdot+} \overset{K_{18}}{\rightleftharpoons} (\mathrm{Th}-\mathrm{AnH})^{2+} + \mathrm{DBO} \tag{18}$$
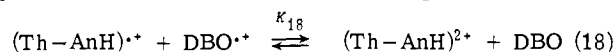
The latter being the case, it is readily seen that if a 1:1 mixture of $\mathrm{Th}^{\cdot+}$-$\mathrm{DBO}^{\cdot+}$ were allowed to react with AnH, eq 13-15 suggest that the rate of the reaction should be greatly enhanced by the presence of $\mathrm{DBO}^{\cdot+}$ because of the greater steady state concentration of $(\mathrm{Th}-\mathrm{AnH})^{2+}$. It was found that the presence of an equivalent amount of $\mathrm{DBO}^{\cdot+}$ increased the rate of the anisylation of $\mathrm{Th}^{\cdot+}$ by a factor of about 200, and the stoichiometry of the reaction was that predicted, i.e., eq 19. These results strongly support our mechanism assignment.

$$\mathrm{Th}^{\cdot+} + \mathrm{DBO}^{\cdot+} + \mathrm{AnH} \longrightarrow (\mathrm{Th}-\mathrm{An})^+ + \mathrm{DBO} + \mathrm{H}^+ \tag{19}$$
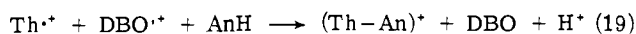
It is worthwhile to consider what the effect of $\mathrm{DBO}^{\cdot+}$ would be on other possible mechanisms. If the function of $\mathrm{DBO}^{\cdot+}$ were only to maintain a higher $[\mathrm{Th}^{\cdot+}]$ (eq 20), the

$$\mathrm{Th} + \mathrm{DBO}^{\cdot+} \rightleftharpoons \mathrm{Th}^{\cdot+} + \mathrm{DBO} \tag{20}$$
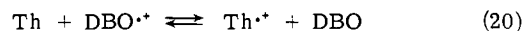
rate would be enhanced but would not be more than a factor of 2. The predicted effect on the disproportionation mechanism is about the same as for the complexation mechanism since K_{21} is approximately 10^3 times as great as K_6.

$$\mathrm{Th}^{\cdot+} + \mathrm{DBO}^{\cdot+} \rightleftharpoons \mathrm{Th}^{2+} + \mathrm{DBO} \tag{21}$$
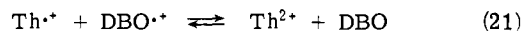
However, disproportionation has been ruled out in previous discussion. It is difficult to see any possible effect of $\mathrm{DBO}^{\cdot+}$ on the dimer dication mechanism.

Further support for eq 13-15 was obtained from runs conducted at very low cation radical concentrations. When $[\mathrm{Th}^{\cdot+}]$ was of the order of $10^{-5}\ M$, the kinetic data gave very poor fit to second order plots, but good first-order plots were obtained from data from either acetonitrile (Table IV) or dichloromethane; under conditions where first-order kinetics in $[\mathrm{Th}^{\cdot+}]$ were observed, the reaction was also first order in [AnH]. The change in kinetic order with changing $[\mathrm{Th}^{\cdot+}]$ can readily be understood upon consideration of eq 14. When the concentration of $\mathrm{Th}^{\cdot+}$ is of the order of $10^{-5}\ M$, and if the equilibrium concentration of the complex $(\mathrm{Th}-\mathrm{AnH})^{\cdot+}$ is of the order of 0.1% of the total radical ion concentration[29] or of the order of $10^{-8}\ M$, this step would be expected to be very slow. If another reaction pathway exists for the initial complex, not involving $\mathrm{Th}^{\cdot+}$, it would be expected to be of much greater importance as step 11 becomes slower. In fact, under the conditions where pseudo-first-order kinetics were observed, the reaction takes an altogether different course resulting in total reduction of

Th$\cdot^+$. Thus, the competing step can be formulated as follows (eq 22):

$$(\text{Th}-\text{AnH})\cdot^+ \underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} \text{Th} + \text{AnH}\cdot^+ \qquad (22)$$
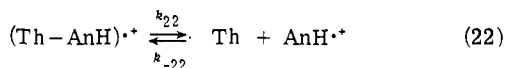
Since the direct comparison of first- and second-order rate constants is meaningless, it is necessary to convert the data into a common dimension. The latter can be conveniently accomplished by a comparison of the half-lives obtained from the first- and second-order rate constants. Since the first-order half-life is concentration independent, a constant value is expected throughout the concentration range. On the other hand, a tenfold decrease in [Th$\cdot^+$] is accomplished by a tenfold increase in the half-life according to the second-order mechanism. The half-life of Th$\cdot^+$ is equal to 450 sec by either mechanism when the concentration is 3.1×10^{-5} M. This clearly accounts for the fact that data in the concentration range of about 7×10^{-5} to 3×10^{-5} M gave poor second- and first-order plots since both mechanisms are operative in this range. If further reaction of AnH$\cdot^+$ (eq 23) is rate determining, application of the steady-state approximation of AnH$\cdot^+$ results in eq 24 for the first-order reaction. The low concentrations necessary for the observa-

$$\text{An}\cdot^+ \overset{k_{23}}{\longrightarrow} \text{products} \qquad (23)$$
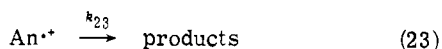
$$\frac{-\text{d}[\text{Th}\cdot^+]}{\text{d}t} = \frac{k_{24}K_{13}[\text{Th}\cdot^+][\text{AnH}]}{k_{23}/k_{-22} \div [\text{Th}]} \qquad (24)$$

tion of first-order kinetics precluded the observation of products derived from anisole. However, electrochemical techniques indicate that the reduction of Th$\cdot^+$ is quantitative. The products of the reaction between DBO$\cdot^+$ and AnH have been shown to be DBO and 4,4'-dimethoxybiphenyl cation radical when the reaction is carried out in dichloromethane-TFA-TFAn (97:2:1), and it is reasonable to assume that the fate of the anisole cation radical is similar in this case, although at the very low concentrations involved other reactions may become important.

In conclusion, the complexation mechanism (eq 13–15) fits all the observed experimental data for the anisylation of Th$\cdot^+$ and appears to be a reasonable alternative to the disproportionation mechanism previously proposed,[10] and ruled out by this work.

Experimental Section

Acetonitrile and dichloromethane were reagent grade and passed through a column of neutral alumina (Woelm W 200) immediately before use. Trifluoroacetic acid anhydride was Fluka (Purum grade) and used as obtained.

The apparatus used for voltammetric measurements has been described.[30] The cell used both for the kinetic study and for the preparation of the cation radical solutions was a cylindrical, round-bottom, jacketed container with openings for the auxiliary electrode compartment, reference electrode, inert gas supply, thermometer, and a Beckman rotating disk electrode. The temperature was controlled either with tap water or with a cryostat. The cation radical solutions were prepared by partial oxidation of solutions of thianthrene in the solvent systems. Oxidations were carried out at constant current (12.5 mA) at a large area platinum gauze electrode. Current was passed for a time calculated to give the desired concentration of cation radical. The concentration of cation radical was determined exactly after oxidation by the magnitude of the limiting current at the rotating disk electrode. The limiting current was followed as a function of time for several minutes, and no decrease in cation radical concentration was observed before adding anisole. The procedure used for carrying out the kinetic runs was that previously described.[8]

Anisylation of Th$\cdot^+$ in the Presence of DBO$\cdot^+$. Solutions of DBO (0.9–1.3 mM) were subjected to constant current electrolysis to achieve partial conversion to DBO$\cdot^+$ (0.4–0.6 mM) in MeCN-TFAn (99:1) containing NaClO$_4$ (0.1 M). The exact concentrations of DBO and DBO$\cdot^+$ were then determined by rde voltammetry. Enough Th in the solvent system was added to give equal concentrations of Th$\cdot^+$ and DBO$\cdot^+$. After AnH was added, the decay of reduction current due to the total cation radical concentration was followed at the rde. Voltammetric measurements at the end of the run showed that all the Th was consumed, and that none of the DBO was consumed.

(Th–An)$^+$ClO$_4^-$. Thianthrene (10.0 mmol) in acetonitrile-TFAn (99:1) containing NaClO$_4$ (0.1 M) and anisole (50 mmol) was subjected to anodic oxidation at a platinum gauze electrode at a constant current of 200 mA in a two-compartment cell cooled by tap water. After 2.0 faradays/mol had passed (161 min), dichloromethane (200 ml) was added to the anolyte, and the organic phase was extracted with three 100-ml portions of water. After drying over molecular sieves, the dichloromethane solution was concentrated to about 10 ml, and the product was precipitated by adding CCl$_4$ (87% yield). The product was recrystallized from CH$_2$Cl$_2$-CCl$_4$: nmr δ 8.4 (m, 2 H), 7.8 (m, 6 H), 7.1 (AA'BB', 4 H), and 3.8 (s, 3 H) in CDCl$_3$.

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(25) This treatment assumes that equilibrium 13 is fast compared with equilibrium 14. The latter assumption does not seem unreasonable since (13) only involves an encounter complexation and dissociation, while step 14 involves the formation of an encounter complex, internal electron transfer to give a new encounter complex which dissociates.
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(29) The equilibrium concentration cannot be much greater than 0.1% at this total concentration since it cannot be detected at even higher radical ion concentrations.
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