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(4) Thiol **2** shows in the ¹H NMR spectrum C–H/S–H coupling (8.0 Hz) reminiscent of the well-studied C–H/O–H coupling in di-*tert*-butylcarbinol. See L. K. Patterson and R. M. Hammaker, *J. Phys. Chem.*, **70**, 3745 (1966), and succeeding papers.

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Reactions of Cation Radicals of EE Systems. 5. Acid–Base Equilibria in Nucleophilic Reactions of Pyridine and Water with Thianthrene Cation Radical[1a]

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The role of cation radical/nucleophile adduct deprotonation equilibria in the reactions of thianthrene cation radical (Th·⁺) with pyridine and water in acetonitrile solution has been examined using stopped-flow and electrochemical techniques. In both reactions reversible nucleophilic attack and adduct formation at a sulfur site on Th·⁺ is proposed as the first step in a general half-regeneration scheme. Rate-determining electron transfer involves reaction between adduct (oxidant) and deprotonated adduct in the case of a protic nucleophile (e.g., water). In the case of an aprotic nucleophile (e.g., pyridine) the rate-determining encounter is between a nonadducted cation radical and adduct with the adduct functioning here as the reducing agent. The formation of the product of *both* reactions, thianthrene 5-oxide, is discussed in terms of the relative stabilities of the oxidized forms of these cation radical/nucleophile adducts.

Recent studies of the kinetics and mechanisms of the reactions of the 9,10-diphenylanthracene (DPA) cation radical (DPA·⁺) with various nucleophiles and reducing agents[1] suggest that a half-regeneration mechanism[2] predominates in all cases where addition products are observed. Although this scheme is operative in the cases examined thus far, reactions of DPA·⁺ with certain nucleophiles (e.g., chloride)[1d] have exhibited reaction dynamics which are second order in cation radical concentration. These observations are accounted for within the half-regeneration pathway in terms of rapid, reversible cation radical/nucleophile adduct formation which precedes rate-determining electron transfer from this adduct to a second ion radical. By comparison protic nucleophiles (e.g., water) in reaction with DPA·⁺ show a first-order dependence of rate on both nucleophile and cation radical concentration,[3,4] indicative of rate-determining adduct formation. Such observations invite speculation concerning the role of ion radical/nucleophile adduct deprotonation steps and the extent to which processes of this type may influence the observed dynamics of a particular reaction.

An ideal system through which this role can be probed is afforded by the cation radical derived from thianthrene (Th). While the hydrolysis of the thianthrene cation radical (Th·⁺) is known to be second order with respect to radical ion,[5,6] the corresponding anisylation of this species has been accounted for via a half-regeneration mechanism which exhibits concentration-dependent reaction order.[7] This mechanism involves adduction equilibria of the type noted in the chlorination of DPA.[1d]

The reaction of pyridine with Th·⁺ in neat pyridine affords the *ring-substituted* product[8] Th(Py)⁺ in which charge relief for this two-electron deficient species has occurred via substrate proton loss. Alternatively, the hydrolysis (protic nucleophile) of Th·⁺ affords the addition product, thianthrene 5-oxide (ThO),[5,6] in which charge relief has been attained by

ThO   Th(Py)⁺
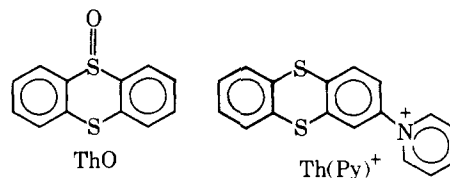
discharge of nucleophile protons. The nucleophiles pyridine and water were therefore selected for a comparative evaluation of the mechanistic effects exerted by protic and aprotic nucleophiles upon their respective reactions with the cation radical of thianthrene.
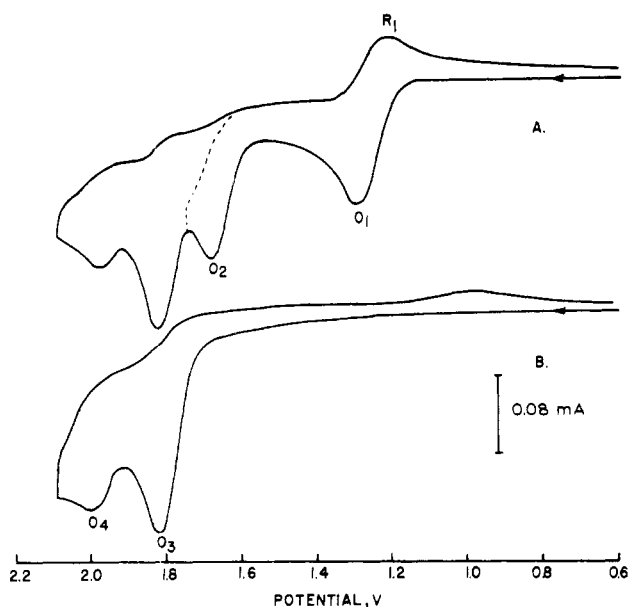
Figure 1. Anodic voltammetry of acetonitrile containing 0.10 M tetraethylammonium perchlorate (TEAP) and 1.0 mM Th (curve A) or 1.0 mM ThO (curve B). Scan rate 150 mV/s.

This report details kinetic results and product analyses which offer insight into the role of acid–base reactions of cation radical/nucleophile adducts and points to the necessity of such considerations in the study of the addition reactions of cation radicals derived from EE substrates.[9]

Results and Discussion

Reaction of Th·+ with Water. The cyclic voltammetric behavior of Th at a platinum electrode in anhydrous acetonitrile is shown in Figure 1. The oxidative process observed at a potential of +1.25 V (O$_1$, curve A) is attributed to the oxidation of Th to Th·+ (eq 1).

$$Th \rightleftharpoons Th\cdot^+ + e^- \qquad (1)$$

$$Th\cdot^+ \rightleftharpoons Th^{2+} + e^- \qquad (2)$$

Upon scanning to more anodic potentials a second monoelectronic oxidation wave is observed with a peak at +1.65 V (O$_2$) corresponding to the formation of dication (Th^{2+}) from cation radical (eq 2). Scan reversal at this point shows no peak for the reduction of the dication formed at O$_2$; however, the stability of the cation radical in this medium is noted by the presence of the cathodic wave (R$_1$) for cation radical reduction. The absence of the wave corresponding to dication reduction may be taken as a measure of its reactivity in this solvent-supporting electrolyte system. Although residual water is present at very low concentrations (ca. 1–3 mM) in this rigorously dried solvent, a sufficient quantity is present to cause the rapid formation of the monoxide (ThO, eq 3)

$$Th^{2+} + H_2O \xrightarrow{fast} ThO + 2H^+ \qquad (3)$$
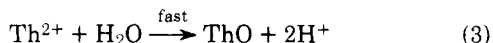
from dication. The ThO species is characterized by its oxidative electrochemistry[10] (O$_3$ and O$_4$) which is evident in both voltammograms of Figure 1. As water is incrementally added to the solution, O$_1$, O$_3$, and O$_4$ increase in height at the expense of O$_2$ and R$_1$.[11] O$_1$ is enhanced due to the regenerative nature of the overall reaction (eq 4).[5,6]

$$2Th\cdot^+ + H_2O \rightarrow ThO + Th + 2H^+ \qquad (4)$$
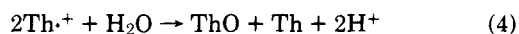
By carrying out exhaustive electrolyses of wet acetonitrile solutions of Th at a potential of +1.40 V, one notes the passage
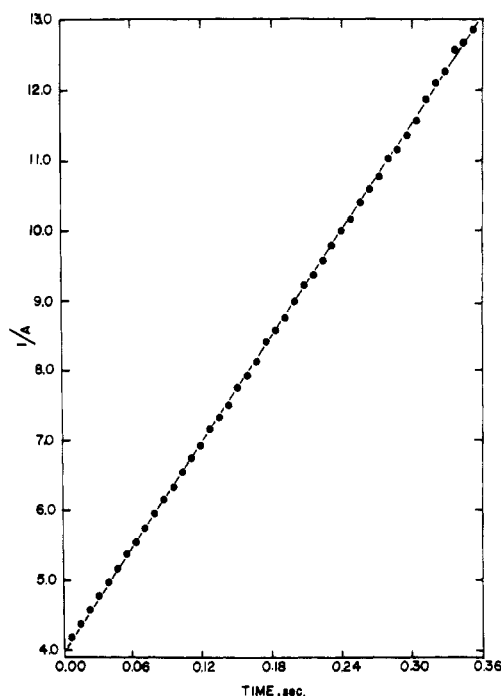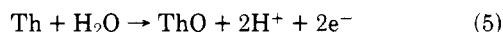

Figure 2. Second-order kinetic plot for the reaction of electrochemically generated Th·+ with water (0.20 M) in acetonitrile containing 0.10 M TEAP and 1.50 mM Th. $T = 25.0 (\pm 0.1)$ °C.

of charge corresponding to 2 Faradays/mol of Th originally present (eq 5).

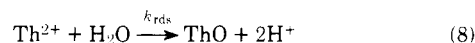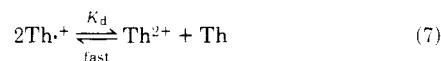$$Th + H_2O \rightarrow ThO + 2H^+ + 2e^- \qquad (5)$$

Following electrolysis, the anolyte shows the characteristic response of ThO (Figure 1, curve B).

Either of two possible mechanisms for the reaction of Th·+ with H$_2$O can account for the aforementioned observations. Scheme I, the disproportionation mechanism, has been argued by Murata and Shine[5,6] on the basis of kinetic results indicating an experimental rate law of the form[13]
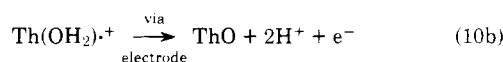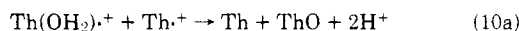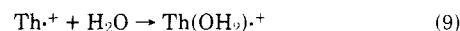
$$-\frac{d[Th\cdot^+]}{dt} = k_{app} \frac{[Th\cdot^+]^2[H_2O]}{[Th]} \qquad (6)$$

Scheme I

$$2Th\cdot^+ \underset{fast}{\overset{K_d}{\rightleftharpoons}} Th^{2+} + Th \qquad (7)$$

$$Th^{2+} + H_2O \xrightarrow{k_{rds}} ThO + 2H^+ \qquad (8)$$

According to this scheme the oxidized form of Th which undergoes nucleophilic attack by H$_2$O is the *dication*. Parker and Eberson subsequently presented evidence which indicated that the *cation radical* reacts directly with the nucleophile.[14] Their observations support the half-regeneration mechanism[3,4] shown in Scheme II.

Scheme II

$$Th\cdot^+ + H_2O \rightarrow Th(OH_2)\cdot^+ \qquad (9)$$

$$Th(OH_2)\cdot^+ + Th\cdot^+ \rightarrow Th + ThO + 2H^+ \qquad (10a)$$

$$Th(OH_2)\cdot^+ \xrightarrow[electrode]{via} ThO + 2H^+ + e^- \qquad (10b)$$

Included here are two routes for the oxidation of the Th(OH$_2$)·+ intermediate. The first (eq 10a) represents the homogeneous pathway (half-regeneration mechanism) while the second (eq 10b) shows the oxidation of Th(OH$_2$)·+ as proceeding heterogeneously (ECE mechanism).[2]

Table I. Stopped-Flow Kinetic Results for the Hydrolysis of Thianthrene Cation Radical at 25.0 ($\pm$ 0.1) °C

Series	[H$_2$O], M	Source[a] of Th·$^+$	[Th], $\times 10^3$ M	[ThO], $\times 10^3$ M	Replicates	k_{obsd},[b] A^{-1} s^{-1}
1	0.050	E	0.61	0.00	9	0.427 ($\pm$0.023)[c]
2	0.056	S	0.00	0.00	5	0.365 ($\pm$0.007)
3	0.100	E	0.61	0.00	8	3.42 ($\pm$0.23)
4	0.150	E	0.60	0.00	7	7.53 ($\pm$0.33)
5	0.150	E	0.06	0.00	6	7.23 ($\pm$0.33)
6	0.200	E	1.50	0.00	7	25.3 ($\pm$1.5)
7	0.200	E	0.61	0.00	5	19.3 ($\pm$0.6)
8	0.200	E	0.06	0.00	10	17.9 ($\pm$1.5)
9	0.200	E	0.00	0.00	10	20.4 ($\pm$0.7)
10	0.200	S	0.00	0.00	10	26.4 ($\pm$2.8)
11	0.200	S	0.61	0.52	8	26.5 ($\pm$0.9)
12	0.333	S	0.00	0.00	6	105 ($\pm$9)
13	0.400	E	0.61	0.00	7	195 ($\pm$5)
14	0.500	E	3.00	0.00	5	397 ($\pm$13)
15	0.556	S	0.00	0.00	10	312 ($\pm$23)
16	1.00	E	0.61	0.00	8	3430 ($\pm$80)

[a] Source of Th·$^+$ either via electrolysis (E) of Th solution or from solution of Th·$^+$ ClO$_4^-$ salt (S). Both Th·$^+$ and H$_2$O reactant solutions contained 0.10 M tetraethylammonium perchlorate to maintain constant ionic strength. Initial [Th·$^+$] ranged between 1×10^{-5} and 5×10^{-5} M. [b] k_{obsd} defined as the slope of a plot of $1/A_{546}$ vs. time. All data treated for at least 2 half-lives. Correlation coefficients were typically 0.9995, and in all cases exceeded 0.9990. [c] Parentheses contain one standard deviation.
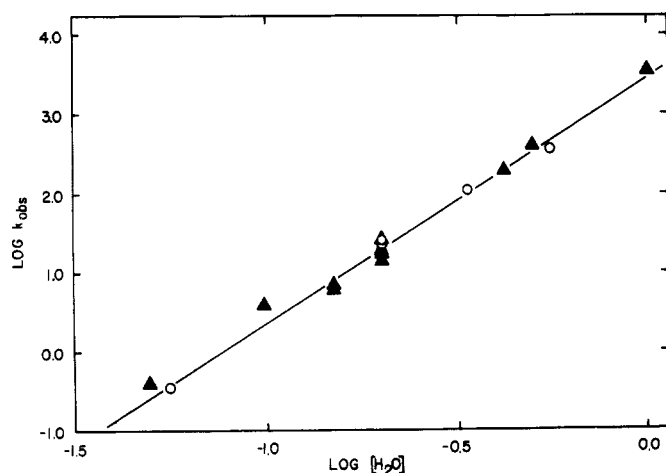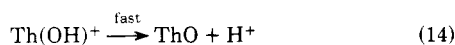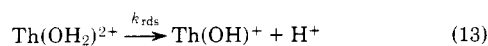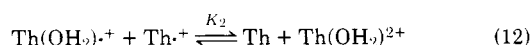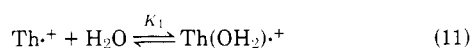

Figure 3. Dependence of second-order rate constant on water concentration for the reaction of Th·$^+$ with aqueous acetonitrile. k_{obsd} defined as slope of second-order kinetic plot (Figure 2). ▲, Th·$^+$ from electrogeneration; ○, Th·$^+$ from Th·$^+$·ClO$_4^-$ salt. T = 25.0 ($\pm$ 0.1) °C.

Scheme III outlines a half-regeneration pathway which affords a rate law of a form which accounts for the observed kinetics.[4,5]

Scheme III

$$\text{Th·}^+ + \text{H}_2\text{O} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Th(OH}_2)\text{·}^+ \tag{11}$$

$$\text{Th(OH}_2)\text{·}^+ + \text{Th·}^+ \underset{}{\overset{K_2}{\rightleftharpoons}} \text{Th} + \text{Th(OH}_2)^{2+} \tag{12}$$

$$\text{Th(OH}_2)^{2+} \xrightarrow{k_{rds}} \text{Th(OH)}^+ + \text{H}^+ \tag{13}$$

$$\text{Th(OH)}^+ \xrightarrow{\text{fast}} \text{ThO} + \text{H}^+ \tag{14}$$

As depicted in Figure 2, stopped-flow experiments gave data indicative of a clean second-order decay of Th·$^+$ upon reaction with aqueous acetonitrile. However, description of the hydrolysis of Th·$^+$ in terms of Scheme III was soon abandoned for reasons which become obvious upon close examination of the data presented in Table I. As reflected in series 6–10, there

can be no statistically significant dependence of reaction rate on the concentration of Th.[15] Series 11 provides evidence that the same is true for ThO, the second product of the reaction.
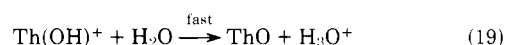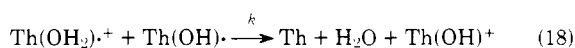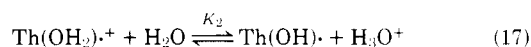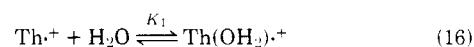
The most striking feature of the data presented in this table is, however, the unusual dependence of Th·$^+$ consumption on the concentration of water. A plot of log k_{obsd} vs. log [H$_2$O] is given in Figure 3. The relationship is linear and gives rise to a slope of 2.99 ($\pm$ 0.10) indicating a third-order dependence of reaction rate on water concentration. In concert, these observations result in an experimental rate law (eq 15)

$$-\frac{d[\text{Th·}^+]}{dt} = k_{app}[\text{Th·}^+]^2[\text{H}_2\text{O}]^3 \tag{15}$$

which is second order in Th·$^+$, third order in H$_2$O, and independent of precursor and ThO concentrations.

Since a single molecule of water ultimately undergoes addition to one of the cation radicals consumed in the reaction, it must be concluded that the others perform some transient function to promote the progress of the reaction. The following pathway is proposed:

Scheme IV

$$\text{Th·}^+ + \text{H}_2\text{O} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Th(OH}_2)\text{·}^+ \tag{16}$$

$$\text{Th(OH}_2)\text{·}^+ + \text{H}_2\text{O} \underset{}{\overset{K_2}{\rightleftharpoons}} \text{Th(OH)·} + \text{H}_3\text{O}^+ \tag{17}$$

$$\text{Th(OH}_2)\text{·}^+ + \text{Th(OH)·} \xrightarrow{k} \text{Th} + \text{H}_2\text{O} + \text{Th(OH)}^+ \tag{18}$$

$$\text{Th(OH)}^+ + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{ThO} + \text{H}_3\text{O}^+ \tag{19}$$

The thianthrene cation radical is rapidly and reversibly complexed by water to form the Th(OH$_2$)·$^+$ adduct. This adduction equilibrium (eq 16) very strongly favors the complex, which in turn is involved in yet another rapid equilibrium in which adduct is deprotonated to form the Th(OH)· radical. The rate-determining step, then, consists of electron transfer from Th(OH)· to cation radical–nucleophile adduct (eq 18). The products of this rate-determining redox reaction are precursor, water, and protonated oxide which in the presence of excess base (H$_2$O) is rapidly deprotonated (eq 19).[16]

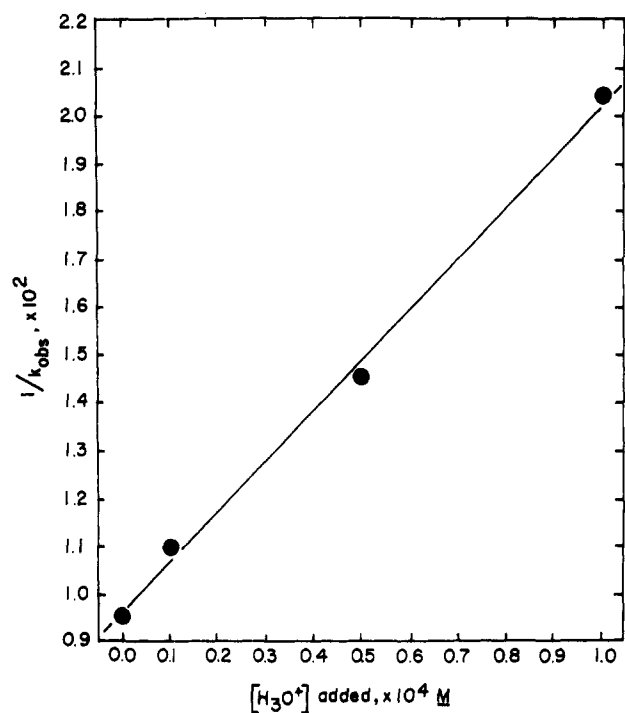On a stoichiometric basis two cation radicals are consumed

Figure 4. Dependence of second-order rate constant on added acid concentration. Added acid was $HClO_4$. $Th^{.+}$ from $Th^{.+}ClO_4^-$ salt and $[H_2O] = 0.33$ M in all cases. $T = 25.0 (\pm 0.1)$ °C.
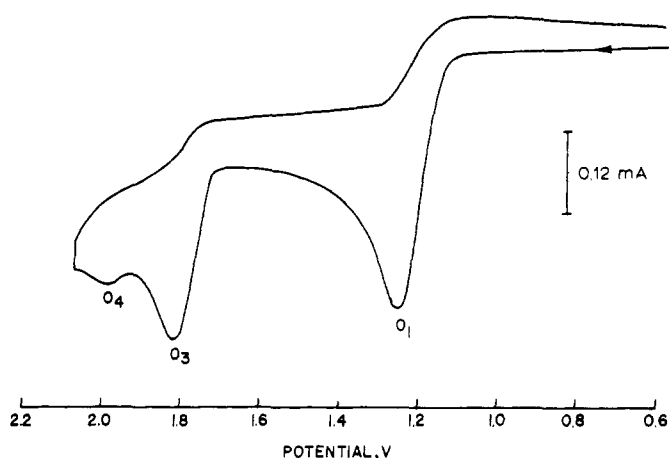

Figure 5. Anodic voltammetry of Th (1.0 mM) in the presence of excess Py (3.0 mM) and TEAP (0.10 M) in acetonitrile. Scan rate 150 mV/s.
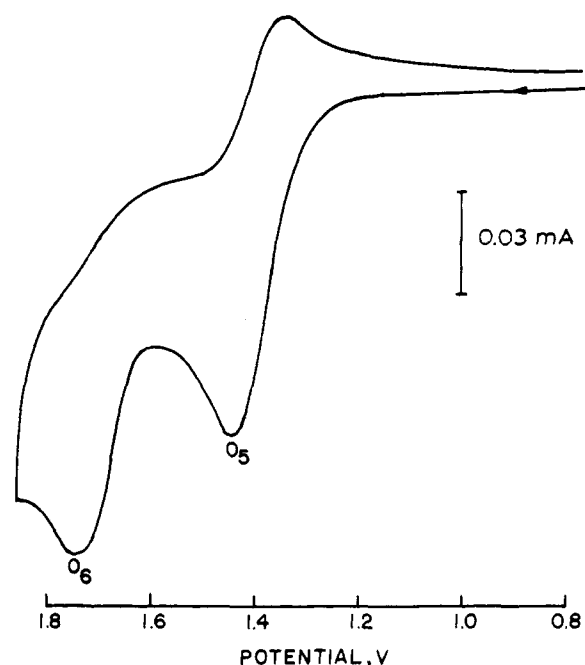
for each $Th(OH)^.$ which is involved in a rate-determining encounter, i.e., one from which the $Th(OH)^.$ species was formed and a second from which the oxidizing agent, $Th(OH_2)^{.+}$, was formed. One may write

$$-\frac{d[Th^{.+}]}{dt} = -2\frac{d[Th(OH)^.]}{dt} \qquad (20)$$

By virtue of its involvement in the rate-determining step, eq 18, the rate of disappearance of $Th(OH)^.$ may be expressed as

$$-\frac{d[Th(OH)^.]}{dt} = k[Th(OH)^.][Th(OH_2)^{.+}] \qquad (21)$$

The equilibrium expressions for the processes preceding the rate-determining step are given by

$$K_1 = \frac{[Th(OH_2)^{.+}]}{[Th^{.+}][H_2O]} \qquad (22)$$

$$K_2 = \frac{[Th(OH)^.][H_3O^+]}{[Th(OH_2)^{.+}][H_2O]} \qquad (23)$$

Appropriate rearrangement of eq 22 and 23 and substitution with eq 20 into eq 21 results in a form of the rate law for Scheme IV which is compatible with the experimental results.

$$-\frac{d[Th^{.+}]}{dt} = \frac{2kK_1{}^2K_2[Th^{.+}]^2[H_2O]^3}{[H_3O^+]} \qquad (24)$$

Thus, for the 131 experiments reported in Table I, $kK_1{}^2K_2/[H_3O^+]$ evaluates to $4.64 (\pm 1.04) \times 10^7$ M^{-4} s^{-1}.

If the hydrolysis of $Th^{.+}$ is correctly accounted for by Scheme IV, then a depression of reaction rate should be noted upon the addition of hydronium ion to the reaction mixture. Such experiments were conducted and the results are shown in Figure 4. The inverse first-order dependence of reaction rate on added H_3O^+ is clearly evident from these data and lends further credence to the proposed mechanism.

Reaction of Th$^{.+}$ with Pyridine. The cyclic voltammetric behavior of Th in the presence of a twofold excess of pyridine

Figure 6. Anodic voltammetry of 1.0 mM Th(Py)$^+$ClO$_4^-$ and 0.10 M TEAP in acetonitrile. Scan rate 110 mV/s.

at moderate scan rate is shown in Figure 5. A catalytic current[12] indicative of Th regeneration as a consequence of Th$^{.+}$ reaction is noted at O_1 where Th is oxidized to Th$^{.+}$ and the characteristic voltammetry of the monoxide is also observed (O_3 and O_4). Seemingly, the product of the anodic oxidation of Th where Py is present is the oxide, yet Shine et al. have reported the reaction of Th$^{.+}$ with Py in both nitromethane and neat Py to yield the N-(2-thianthrenyl)pyridinium ion [Th(Py)$^+$].[8] Since the assignment of voltammetric peaks to particular intermediates or products is often tenuous, authentic Th(Py)$^+$ was prepared[8] and isolated as the perchlorate salt for use in cyclic voltammetric characterization of this species. The voltammetry of acetonitrile solutions of this ion is shown in Figure 6. One observes a morphology similar to that of Th; however, the two anodic peaks (O_5 and O_6) appear at decidedly different potentials (+1.45 and +1.74 V) than the corresponding peaks (O_1 and O_2) of Th. Reexamination of Figure 5 shows the Th(Py)$^+$ ion to be absent in this scan and it is apparent that this species is not detected under these conditions. Analysis of the products isolated from the reaction
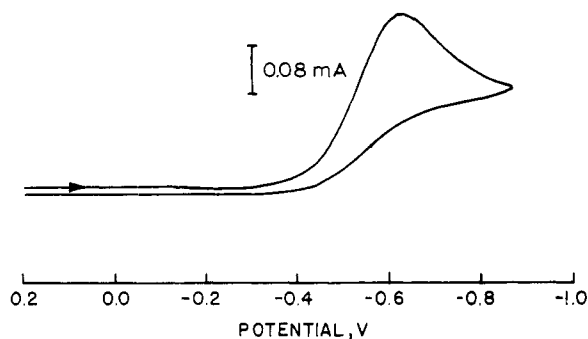
Figure 7. Cathodic voltammetry of PyHClO$_4$ (1.0 mM) and TEAP (0.10 M) in acetonitrile. Scan rate 120 mV/s.

of the perchlorate salt of Th$\cdot^+$ with Py (0.50 M) carried out in acetonitrile also revealed the lack of a detectable quantity of the Th(Py)$^+$ ion (as perchlorate). ThO and Th, in addition to pyridinium perchlorate (PyHClO$_4$), were the products isolated.

This ambiguity between the reaction conducted in acetonitrile and that carried out in neat pyridine or nitromethane was probed further using controlled potential coulometric procedures to elucidate the stoichiometry of the acetonitrile reaction. Exhaustive electrolysis (+1.40 V) of acetonitrile solutions containing both Th and Py revealed the release of 1.99 ($\pm$ 0.01) electrons per molecule of Th present in the anolyte. The anodic voltammetry of this solution following electrolysis showed only the presence of the ThO waves while excursions to cathodic potentials showed the presence of a wave (Figure 7) for the reduction of pyridinium ion (PyH$^+$). It was found that this cathodic wave could be used to quantitate the PyH$^+$ formed during the electrolysis conducted at +1.40 V by carrying out a subsequent, reductive electrolysis of the anolyte from the aforementioned electrolysis at a potential of -0.80 V.[18] Such procedures were performed and after electrolysis at +1.40 V, 2.02 ($\pm$ 0.01) mol of PyH$^+$ was found to be present per mole of Th originally taken. In toto, these observations lead to the formulation of the stoichiometry given by eq 25 for the electrolysis of Th in acetonitrile solution containing Py.

$$\text{Th} + 2\text{Py} + \text{H}_2\text{O} \rightarrow \text{ThO} + 2\text{PyH}^+ + 2e^- \qquad (25)$$
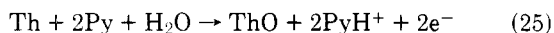
These results suggested that residual water (ca. 1–3 mM) present in the "anhydrous" acetonitrile employed for these studies contributed to the absence of the Th(Py)$^+$ ion. A series of experiments was then undertaken in which trifluoroacetic anhydride (TFAn) was added to the solvent to scavenge the residual water.[20] However, reaction of the perchlorate salt of Th$\cdot^+$ with 0.50 M pyridine in acetonitrile containing 4% TFAn (v/v) again failed to afford a detectable quantity of Th(Py)$^+$ ion. Rather, workup of this reaction mixture indicated the stoichiometry of eq 26

$$2\text{Th}\cdot^+ \text{ClO}_4^- + \text{H}_2\text{O} + 2\text{Py}$$
$$\rightarrow \text{Th} + \text{ThO} + 2\text{PyHClO}_4 \quad (26)$$
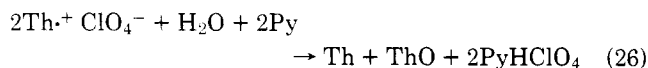
where the respective yields of Th, ThO, and PyHClO$_4$ were 76, 79, and 74%.

It had been assumed that residual water in the acetonitrile would be irreversibly *reacted* upon addition of TFAn. However, subsequent gas chromatographic analysis of the mixed solvent showed the presence of water. Furthermore, its concentration in the TFAn/acetonitrile was at essentially the same level noted in acetonitrile free of TFAn and leads to the conclusion that the water-scavenging properties of the TFAn are attributable to the *selective solvation* (i.e., complexation) of water by the TFAn in this medium.[22]
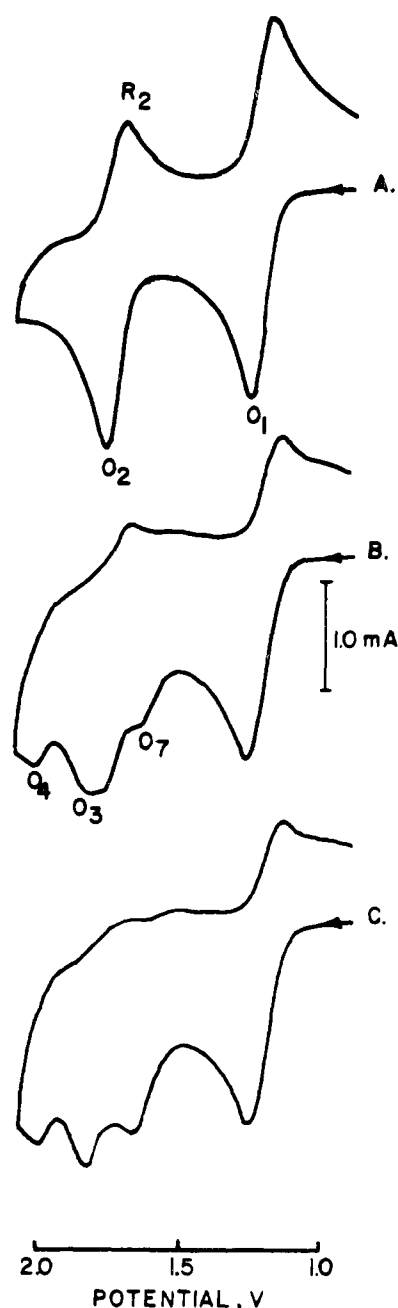

Figure 8. Fast cyclic voltammetry of 1.0 mM Th and 0.20 M TEAP in 4% TFAn/acetonitrile: (A) no Py added; (B) 0.93 mM Py added; (C) 1.55 mM Py added. Scan rate 35 V/s.

A series of fast (high scan rate) cyclic voltammetric experiments was conducted in the TFAn/acetonitrile mixture in order to elucidate the role of Py in this reaction. The voltammograms shown in Figure 8 summarize the results of these investigations. In the absence of Py, the voltammetric behavior of Th in this medium is depicted in curve A of this figure. The presence of the cathodic wave (R$_2$) for the reduction of the relatively stable dication formed during the oxidative scan (O$_2$) is indicative of the ability of the TFAn to effectively reduce the activity of water in the acetonitrile.[20] In the absence of TFAn, R$_2$ is not observed at these scan rates.

The effect of added Py is shown in Figure 8, curves B and C. Firstly, it should be noted that there is no enhancement of the anodic wave due to the oxidation of Th to Th$\cdot^+$ (O$_1$) upon addition of Py. This indicates that *no* Th is regenerated during the time scale of the experiment. Secondly, a new anodic peak appears at O$_7$ and grows with incremental addition of Py as

Table II. Stopped-Flow Kinetic Results for the Reaction of Thianthrene Cation Radical with Pyridine in 4% (v/v) TFAn-Acetonitrile at 25.0 ($\pm$ 0.1) °C

[Th], $\times 10^3$ M	[Th·+]$_0$, $\times 10^5$ M	[Py], $\times 10^3$ M	Replicates	k_{obsd},[a] A^{-1} s^{-1}
0.0	2.95	0.574	10	25.0 ($\pm$0.6)[b]
0.0	3.64	3.44	9	178 ($\pm$4)
0.0	6.09	3.76	5	178 ($\pm$8)
0.0	4.64	5.74	10	282 ($\pm$13)
0.419	3.41	5.74	8	302 ($\pm$8)

[a] k_{obsd} defined as slope of $1/A_{546}$ vs. time. All data treated for 2 half-lives. Correlation coefficients were typically 0.9990 and in all cases exceeded 0.9980. [b] Parentheses contain one standard deviation.
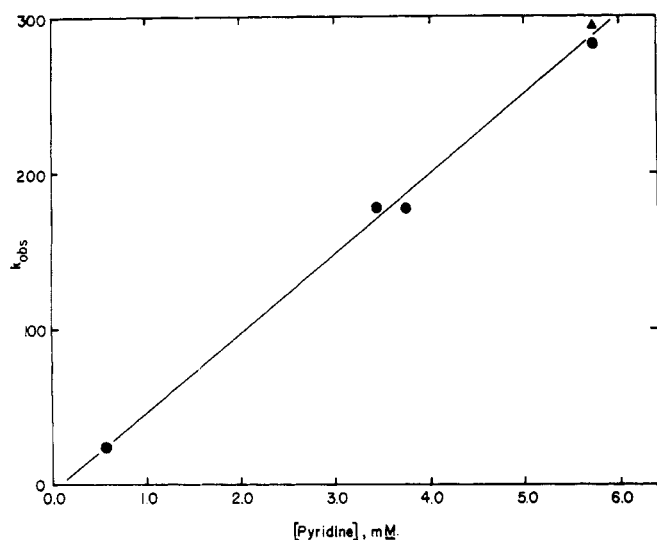

Figure 9. Dependence of observed second-order rate constant for the reaction of Th·+ with Py on concentration of Py. k_{obsd} defined as slope of second-order kinetic plot. In all cases, solvent was 4% TFAn/acetonitrile. Source of Th·+ was Th·+ClO$_4^-$ salt. ●, [Th] = 0.0 mM; ▲, [Th] = 0.42 mM.

do the ThO waves (O$_3$ and O$_4$). These enhancements proceed at the expense of the height of the waves corresponding to the oxidation of Th·+ to Th^{2+} (O$_2$) and its reverse process (R$_2$). These results are interpreted as follows. The species whose oxidation proceeds at O$_7$ is the *sulfur* bonded adduct resulting from reaction of Th·+ with Py:
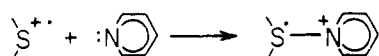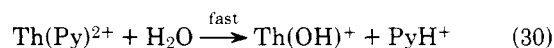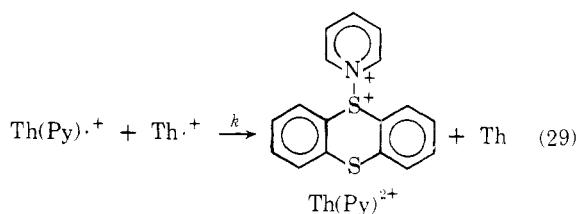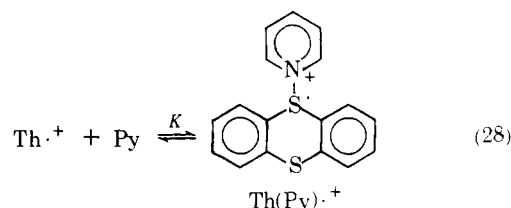

Following *heterogeneous* oxidation (O$_7$), this species is *rapidly* converted to ThO observed at O$_3$ and O$_4$. It is important to note the absence of the peaks attributable to the Th(Py)$^+$ (*carbon* bonded) species (O$_5$ and O$_6$, Figure 6). One must conclude that formation of Th(Py)$^+$ is overwhelmingly less likely than the observed generation of ThO, even in this medium where the reactivity of water has been minimized.

Stopped-flow determination of the Th·+/Py reaction rate in the absence of TFAn clearly indicated second-order dependence on Th·+ concentration. However, rate parameters arising from analysis of these experiments were extremely irreproducible. Reproducibility in these measurements was attained when reactant solutions were prepared in the TFAn/acetonitrile mixed solvent. These data, together with the Py dependence shown in Figure 9, indicate that the experimental rate law takes the form

$$- \frac{d[Th·+]}{dt} = k_{app}[Th·+]^2[Py] \tag{27}$$

The kinetic parameters for the Th·+/Py system, summarized in Table II, attest to the validity of this rate law over a range of Th, Th·+, and Py concentrations.

These stopped-flow results in combination with the observations obtained from the fast cyclic voltammetry of this system lead to the proposition of Scheme V as the mechanism operative in this reaction.

Scheme V

$$Th·+ + Py \overset{K}{\rightleftharpoons} \qquad Th(Py)·+ \tag{28}$$

$$Th(Py)·+ + Th·+ \overset{k}{\longrightarrow} \qquad + Th \qquad Th(Py)^{2+} \tag{29}$$

$$Th(Py)^{2+} + H_2O \overset{fast}{\longrightarrow} Th(OH)^+ + PyH^+ \tag{30}$$

$$Th(OH)^+ + Py \overset{fast}{\longrightarrow} ThO + PyH^+ \tag{31}$$

The rate-determining step (eq 29) involves electron transfer from a pyridine/cation radical sulfur bonded adduct to a nonadducted cation radical. The product of this step [the N–S dication, Th(Py)$^{2+}$] is extremely reactive (more so toward water than is Th^{2+}), undergoing rapid hydrolysis to the protonated oxide [Th(OH)$^+$] and PyH$^+$. Subsequent fast deprotonation by a second Py molecule yields the ultimate addition product, ThO.

In conclusion, the results detailed here suggest the general applicability of a half-regeneration scheme in describing the reactions of thianthrene cation radical with pyridine *and* water in acetonitrile. As carried out in acetonitrile solutions, kinetic results and product analyses support the hypothesis that in both reactions attack of nucleophile occurs at a sulfur site on this cation radical. The inability of the N–S bonded adduct to achieve charge relief via proton loss following further oxidation ultimately leads to the rapid hydrolysis of the oxidized form to yield the monoxide. In both reactions studied, complications of acid–base reactions between cation radical/nucleophile adducts (acids) and nucleophiles (bases) are noted within the framework of the proposed mechanism.

Experimental Section

M. Reagent grade pyridine (J. T. Baker) was distilled at atmospheric pressure from KOH (bp 114–114.5 °C). The concentration of pyridine in acetonitrile solutions was determined by potentiometric titration with perchloric acid in glacial acetic acid.[23] Trifluoroacetic anhydride (TFAn, Fluka A. G., purum grade) was used as received. All solutions used in voltammetry, coulometry, and stopped-flow kinetic measurements were freshly prepared in an inert atmosphere and degassed with prepurified nitrogen.

Pyridinium perchlorate ($PyHClO_4$) was prepared by the combination of stoichiometric amounts of perchloric acid and pyridine in glacial acetic acid,[24] mp 287–289 °C (lit. 287 °C). Thianthrene (Th, Aldrich Chemical Co.) was twice recrystallized from absolute EtOH, mp 156–156.5 °C (lit.[17] 155–157 °C).

Thianthrene 5-oxide (ThO) was prepared according to Fries and Vogt,[25] mp 142.5–143.5 °C (lit. 143 °C). Synthesis of thianthrene cation radical perchlorate ($Th\cdot^+ClO_4^-$) was carried out according to Murata and Shine.[5,6] N-(2-Thianthrenyl)pyridinium perchlorate $[Th(Py)^+ClO_4^-]$ was prepared by the gradual addition of $Th\cdot^+ClO_4^-$ to pyridine with stirring,[8] affording golden yellow crystals, mp 204–206 °C (lit. 206–207 °C). All other chemicals were reagent grade or equivalent.

Reaction of $Th\cdot^+ClO_4^-$ with Pyridine in 4% (v/v) TFAn/Acetonitrile. Reaction and product analyses were performed in a manner analogous to that employing neat pyridine.[8] To a 100-ml volume of 0.50 M pyridine in 4% (v/v) TFAn/acetonitrile was added 0.625 g (1.98 mmol) of $Th\cdot^+ClO_4^-$. The solvent was stripped and ca. 25 ml of nitromethane added. The solids and nitromethane solution were repeatedly extracted with cyclohexane (solids soluabilized during first extraction) until TLC of the extract showed absence of Th and ThO. The combined cyclohexane extracts were concentrated and chromatographed (silica gel/cyclohexane and 95:5 benzene/EtOH). Removal of solvent from the respective fractions yielded 0.163 g of Th (0.75 mmol, 76%) and 0.182 g of ThO (0.78 mmol, 79%). The nitromethane fraction was found to contain 0.262 g (1.46 mmol, 74%) of pyridinium perchlorate.

Apparatus. Electrochemical measurements were carried out using a conventional potentiostat[26] and a two-compartment cell.[1c] All electrode potentials are referred to the aqueous saturated calomel electrode.

A dedicated minicomputer (Data General Corp. NOVA 1200) was interfaced to both the potentiostat and the Durrum Model D-110B stopped-flow spectrophotometer for experimental control as well as data acquisition and subsequent reduction.[1d] Modification of the stopped-flow apparatus to accommodate electrolytic generation of reactants is described elsewhere.[1d] Kinetic determinations were carried out at 25.0 (± 0.1) °C. The molar absorptivity of $Th\cdot^+$ (acetonitrile) was taken to be 8.5×10^3 M^{-1} cm^{-1} at the analytical wavelength (546 nm, λ_{max}) employed for kinetic measurements.[5,6]

Registry No.—$Th\cdot^+$, 34507-27-2; Py, 110-86-1.

References and Notes

(1) (a) Part 4: J. F. Evans and H. N. Blount, *J. Phys. Chem.,* **80**, 1011 (1976); (b) H. N. Blount, *J. Electroanal. Chem.,* **42**, 271 (1973); (c) D. T. Shang and

H. N. Blount, *ibid.,* **54**, 305 (1974); (d) J. F. Evans and H. N. Blount, *J. Org. Chem.,* **41**, 516 (1976).

(2) See ref 1b for a synopsis of mechanisms. The ECE and ECC mechanisms as they apply to electrochemical studies are distinguished on the basis of whether the oxidation of the intermediate (formed upon homogeneous reaction of nucleophile with electrogenerated cation radical) is achieved predominantly by means of *a heterogeneous* (via electrode, ECE) or *a homogeneous* (via a second cation radical, ECC) redox step. In stopped-flow experiments, the absence of the electrode necessarily denies the applicability of the ECE scheme and the half-regeneration mechanism becomes synonomous with its electrochemical counterpart (ECC).

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(9) An EE substrate is defined as a species capable of undergoing two distinct monoelectronic oxidation (or reduction) steps at successively more anodic (or cathodic) potentials. E.g., for the oxidative EE system:

$$A \rightarrow A\cdot^+ + e^- \tag{E_1}$$

$$A\cdot^+ \rightarrow A^{2+} + e^- \tag{E_2}$$

where $E_2 > E_1$.

(10) The processes giving rise to the oxidative currents at O_3 and O_4 are beyond the scope of this paper. Although they are definitive for ThO in this medium, these are complex processes, e.g., O_3 is a 1.24 (± 0.01) electron process per ThO molecule.

(11) O_2 is also noted to shift to more cathodic potentials upon incremental addition of water. This phenomenon is indicative of irreversible homogeneous chemical reaction following electron transfer.[12]

(12) R. S. Nicholson and I. Shain, *Anal. Chem.,* **36**, 706 (1964).

(13) k_{app} necessarily incorporates the equilibrium constant for disproportionation which may be determined from the separation of O_1 and O_2 under conditions where both oxidation steps are chemically reversible (i.e., Th^{2+} is stable). See ref 20 and 21.

(14) V. D. Parker and L. Eberson, *J. Am. Chem. Soc.,* **92**, 7488 (1970).

(15) This observation conflicts with that of Murata and Shine.[5,6] For the reaction conditions reported ($1–5 \times 10^{-5}$ M initial concentrations of $Th\cdot^+$), no inverse dependence of rate on Th concentration has been observed in these laboratories.

(16) The process embodied in eq 19 most probably possesses some degree of reversibility. The protonation of the oxide in strong acid and subsequent $Th\cdot^+$ formation have been noted in these and other[17] laboratories.

(17) H. J. Shine and L. Piette, *J. Am. Chem. Soc.,* **84**, 4798 (1962); H. J. Shine and C. F. Dais, *J. Org. Chem.,* **30**, 2145 (1965).

(18) Authentic $PyHClO_4$ was found to require 0.97 (± 0.01) Faraday/mol for complete reduction at −0.80 V; ostensibly the product is a bipyridyl.[19]

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