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The Hydroxylation of Thianthrene Cation Radical in Buffered Acetonitrile. The Final Word on the Mechanism?

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The kinetics of the hydroxylation of thianthrene cation radical were examined in acetonitrile (AN) and in AN containing 2,6-lutidine (L), trifluoroacetic acid (TFA) and $CF_3CO_2^-LH^+$. The analysis of reaction orders and deuterium kinetic isotope effects resulted in consistency with mechanism (i)–(iv) and three different rate laws depending upon the relative magnitudes of k_{iii}, k_{-iii} and k_{iv}. Only a very small inhibition was observed in the presence of TFA indicating that the acid is not significantly dissociated under the experimental conditions. When present, $CF_3CO_2^-$ was observed to be the strongest base (B) in the system and effectively participated in reaction (ii). The reaction order in water was observed to be as high as 4.5 in neutral AN and to depend upon $[H_2O]$. The high and varying reaction order in water was explained by the effect of hydration equilibrium (v) on the hydronium ion activity. As the water concentration in AN increases H_3O^+ becomes less active and participates less effectively in back reaction (ii). In the absence of water, either pyridine or trifluoroacetate ion participates in reaction (vi) which is reversible during cyclic voltammetry at 100 mV/s.

$$Th^{\cdot +} + H_2O \overset{K_i}{\rightleftarrows} Th^{\cdot}-\overset{+}{O}H_2 \qquad \text{(i)}$$

$$Th^{\cdot}-\overset{+}{O}H_2 + B \overset{K_{ii}}{\rightleftarrows} Th^{\cdot}-OH + BH^+ \qquad \text{(ii)}$$

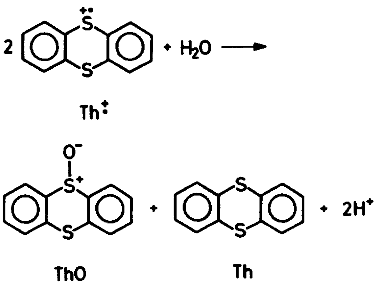
$$Th^{\cdot}-OH + Th^{\cdot +} \underset{k_{-iii}}{\overset{k_{iii}}{\rightleftarrows}} Th^+-OH + Th \qquad \text{(iii)}$$

$$Th^+-OH + B \xrightarrow{k_{iv}} ThO + BH^+ \qquad \text{(iv)}$$

$$H_3O^+ + n\,H_2O \rightleftarrows H_3O^+(H_2O)_n \qquad \text{(v)}$$

$$Th + N \rightleftarrows Th^+-N^{(+)} + 2e^- \qquad \text{(vi)}$$

The reactions of thianthrene cation radical ($Th^{\cdot +}$) with nucleophiles have been the subject of numerous investigations.[1–44] The reaction of $Th^{\cdot +}$ with water (1) was among the first ion radical reactions to be investigated by kinetic techniques.[1,2] The initial investigations led to the conclusion that the dication (Th^{2+}) formed in disproportionation reaction (2) was the intermediate which reacts with water (3) giving rise to rate law (4). This proposal was challenged on the basis of voltammetric experiments and it was suggested that $Th^{\cdot +}$ was the species undergoing reaction with water.[3] An alternative mechanism was suggested which involved steps (5)–(7)



(1)

$$2\,Th^{\cdot +} \overset{K_2}{\rightleftarrows} Th^{2+} + Th \qquad (2)$$

$$Th^{2+} + H_2O \xrightarrow{k_3} ThO + 2\,H^+ \qquad (3)$$

$$\text{Rate} = 2\,k_3K_2[Th^{\cdot +}]^2[H_2O]/[Th] \qquad (4)$$

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$$\mathrm{Th}^{\cdot +} + \mathrm{H_2O} \overset{K_5}{\rightleftarrows} \mathrm{Th}^{\cdot} - \mathrm{OH} + \mathrm{H}^+ \quad (5)$$

$$\mathrm{Th}^{\cdot} - \mathrm{OH} + \mathrm{Th}^{\cdot +} \overset{K_6}{\rightleftarrows} \mathrm{Th}^+ - \mathrm{OH} + \mathrm{Th} \quad (6)$$

$$\mathrm{Th}^+ - \mathrm{OH} \overset{k_7}{\rightarrow} \mathrm{ThO} + \mathrm{H}^+ \quad (7)$$

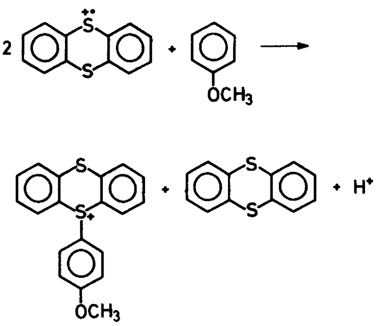
This mechanism had previously been proposed for the conversion of phenoxathiin cation radical to the oxide.[4] It was pointed out that it is difficult to distinguish between the two mechanisms by kinetic measurements.[3] The latter led to attempts to accurately determine the value of K_2 in order to test the feasibility of the disproportionation mechanism.[5,6] The experimental quantities necessary to determine K_2 are the reversible potentials for reactions (8) and (9), *i.e.* E_8^{rev} and E_9^{rev}. The difficulty in obtaining these data lies in the very high reactivity of Th^{2+}.

$$\mathrm{Th} - \mathrm{e}^- \overset{E_8^{\mathrm{rev}}}{\rightleftarrows} \mathrm{Th}^{\cdot +} \quad (8)$$

$$\mathrm{Th}^{\cdot +} - \mathrm{e}^- \overset{E_9^{\mathrm{rev}}}{\rightleftarrows} \mathrm{Th}^{2+} \quad (9)$$

In the initial attempts to determine E_9^{rev}, measurements were carried out in trifluoroacetic acid (TFA) containing $\mathrm{H_2SO_4}$.[5] In this solvent system the difference in reversible potentials for reactions (8) and (9) was observed to be of the order of 780 mV which corresponds to K_2 equal to about 10^{-13}. This prohibitively small value made the disproportionation mechanism appear to be highly unlikely, providing that K_2 is the same in acetonitrile (AN) as in the acidic solvent. However, when it was later discovered that the reversible potential for reaction (9) could be determined in AN by conducting measurements on solutions containing suspended $\mathrm{Al_2O_3}$ it became apparent that K_2 is strongly solvent dependent and the value in AN was observed to be 2.3×10^{-9}.[6] Having a reliable value of K_2, along with the reasonable assumption that back reaction (2) is diffusion controlled, is sufficient to place a maximum of about 2.3 $\mathrm{M^{-1}\,s^{-1}}$ for the observed rate constant for mechanism (2)–(3) using the reasoning developed in related work.[7] The value observed[1,2] was of the order of 0.2 $\mathrm{M^{-1}\,s^{-1}}$, a fact which is consistent with the disproportionation mechanism. Thus, the combination of kinetic and thermodynamic data was not sufficient to distinguish between the two mechanisms in question.

The stalemate encountered in the attempts to elucidate the mechanism of the hydroxylation of $\mathrm{Th}^{\cdot +}$ led to the examination of a related reaction, that of $\mathrm{Th}^{\cdot +}$ with anisole which has the stoichiometry depicted by eqn. (10).[8] A kinetic study of this reaction had also resulted in the proposal of a disproportionation mechanism[9] with a rate law of the same form as (4). However, a more detailed analysis showed that the reaction orders in substrate (Th) and anisole (AnH) are not −1 and 1 as predicted by rapid disproportionation equilibrium followed by rate determining reaction of the dication with anisole but rather more complex with an observed rate constant at a particular [AnH] described by eqn. (11)[8] for reactions conducted in the presence of excess Th and AnH.



(10)

$$1/k_{\mathrm{obs}} = A[\mathrm{Th}]/[\mathrm{AnH}] + B/[\mathrm{AnH}] \quad (11)$$

The important feature of eqn. (11) is that plots of $1/k_{\mathrm{obs}}$ *vs.* the thianthrene concentration are predicted to have intercepts, the magnitude of which are dependent upon [AnH]. On the other hand analysis of the disproportionation mechanism under conditions where (2) cannot be considered to be in equilibrium resulted in expression (12) for the observed rate constant. This relationship predicts an intercept independent upon [AnH].

$$1/k_{\mathrm{obs}} = A'[\mathrm{Th}]/[\mathrm{AnH}] + B' \quad (12)$$

Thus, under the reaction conditions used, the anisylation of $\mathrm{Th}^{\cdot +}$ was shown to take place by a mechanism giving rise to rate law (13), in which k_{obs} is defined in eqn. (11). This rate law is incon-

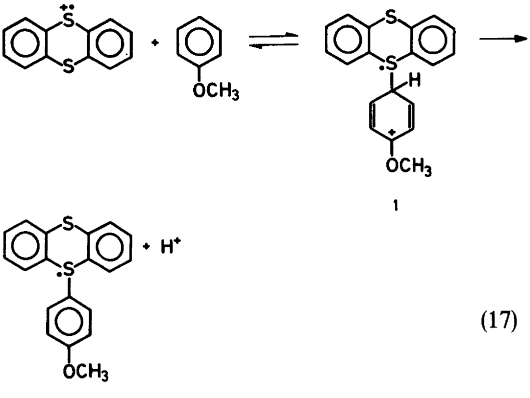
$$\mathrm{Rate} = k_{\mathrm{obs}}[\mathrm{Th}^{\cdot +}]^2 = k_{\mathrm{app}}[\mathrm{Th}^{\cdot +}]^2[\mathrm{AnH}]/(\mathit{constant} + [\mathrm{Th}]) \quad (13)$$

sistent with the disproportionation mechanism. Mechanism (14)–(16) was proposed to account for the kinetic data. The essential features of this mechanism are that covalent bond formation occurs in the dication–anisole complex (16) and that the initial reversible interaction of $Th^{\cdot +}$ and AnH (14) results in a π complex. The overall scheme was called the "complexation mechanism".[8] The reasoning behind the formulation of the mechanism in this manner rather than in the way proposed earlier[3] for the hydroxylation of $Th^{\cdot +}$ as in eqns. (5)–(7) was that *1*, resulting from the reaction of $Th^{\cdot +}$ and anisole would be expected to undergo irreversible proton loss (17) before involvement of the second $Th^{\cdot +}$ moiety. Mechanism (14)–(16) results in rate law (18), which is of the same form as (13).

$$Th^{\cdot +} + AnH \xrightleftharpoons{K_{14}} (Th/AnH)^{\cdot +} \qquad (14)$$

$$(Th/AnH)^{\cdot +} + Th^{\cdot +} \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} (Th/AnH)^{2+} + Th \qquad (15)$$

$$(Th/AnH)^{2+} \xrightarrow{k_{16}} Th^{+}-An + H^{+} \qquad (16)$$



1

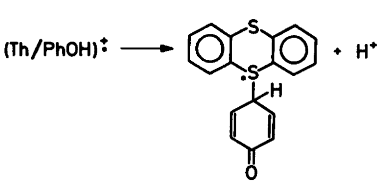
2

(17)

$$\text{Rate} = 2k_{16}K_{14}K_{15}[Th^{\cdot +}]^2[AnH]/(k_{16}/k_{-15} + [Th]) \qquad (18)$$

The reaction of $Th^{\cdot +}$ with phenol (PhOH) in either acetonitrile or dichloromethane was observed to follow rate law (19).[10] It was suggested that the reason for the difference in mechanism with phenol and anisole as the nucleophiles is due to the facile deprotonation of the phenol containing complex accompanied by irreversible covalent bond formation (20), a pathway not available to the anisole complex. The proton transfer from oxygen (20) is suppressed in the presence of TFA and kinetic studies in CH_2Cl_2–TFA resulted in a rate expression identical in form to that when anisole is the nucleophile.[10] This provides very strong support that neither *1*, *2* nor *3* are intermediates in the reactions second order in $Th^{\cdot +}$ and emphasizes the need to invoke the complexation mechanism to explain the kinetic data.

$$\text{Rate} = k_{\text{app}}[Th^{\cdot +}][PhOH] \qquad (19)$$



3

(20)

The hydroxylation of $Th^{\cdot +}$ was reexamined by Evans and Blount[11] using stopped flow kinetic techniques. The reaction was observed to be second order in cation radical, third order in water, and inhibited by acid. The kinetic observations led to the proposal of mechanism (21)–(23) and rate law (24) for the reaction in acetonitrile.

$$Th^{\cdot +} + H_2O \xrightleftharpoons{K_{21}} Th^{\cdot}-\overset{+}{O}H_2 \qquad (21)$$

$$Th^{\cdot}-\overset{+}{O}H_2 + H_2O \xrightleftharpoons{K_{22}} Th^{\cdot}-OH + H_3O^{+} \qquad (22)$$

$$Th^{\cdot}-OH + Th^{\cdot}-\overset{+}{O}H_2 \xrightarrow{k_{23}} \text{products} \qquad (23)$$

$$\text{Rate} = 2k_{23}K_{21}{}^2K_{22}[Th^{\cdot +}]^2[H_2O]^3/[H_3O^{+}] \qquad (24)$$

More recently[12] we have shown that the kinetic analysis used by Evans and Blount[11] involved the improper use of the equilibrium approximation and that mechanism (21)–(23) results in reaction orders in water of either 1 or 2 depending upon the magnitude of K_{21}. Furthermore, kinetic studies[12] of the hydroxylation of $Th^{\cdot +}$ in CH_2Cl_2–TFA resulted in a rate law which is consistent with either the complexation mechanism analogous to (14)–(16) or with a modification of mechanism (5)–(7). The fact that the reaction is first order in water suggests the complexation mechanism since proton loss before the rate determining step would most likely require a molecule of water acting as a base and hence would result in a reaction order of 2 in water.

Another aspect of the study by Evans and Blount[11] which we find highly questionable is the interpretation of experiments carried out in which pyridine was added to acetonitrile-trifluoroacetic anhydride (TFAn) solutions of $\mathrm{Th^{\cdot +}}$ and Th. The addition of TFAn to acetonitrile-supporting electrolyte solutions has been shown to be a highly effective means of removing residual water by virtue of reaction (25).[13] However, such solutions are then several mM in TFA.

$$\mathrm{TFAn + H_2O \rightarrow 2\,TFA} \qquad (25)$$

Evans and Blount[11] disregarded this and interpreted cyclic voltammograms conducted on solutions of Th (1 mM) in acetonitrile-TFAn (4 %) to to which pyridine (Pyr) had been added in concentrations ranging from 0.9 to 1.6 mM as resulting from the reaction of pyridine with $\mathrm{Th^{\cdot +}}$. It is almost inconceivable that there could have been any pyridine present in the solutions due to protonation by TFA. The voltammetric experiments resulted in the proposal that the potential for reaction (26) is of the order of 400 mV positive of that for reaction (8) which leads to a value of about 10^{-7} for K_{27}.

$$\mathrm{Th^{\cdot} - Pyr^+ - e^- \rightleftarrows Th^+ - Pyr^+} \qquad (26)$$

$$\mathrm{Th^{\cdot} - Pyr^+ + Th^{\cdot +} \overset{K_{27}}{\rightleftarrows} Th^+ - Pyr^+ + Th} \qquad (27)$$

But kinetic experiments resulted in apparent second order rate constants of the order of $2\times 10^6\ \mathrm{M^{-1}\,s^{-1}}$ at pyridine concentrations of about 5 mM. The mechanism giving rise to these kinetics was proposed to be (28)–(30). The maximum possible value of k_{29} can be estimated to be $10^3\ \mathrm{M^{-1}\,s^{-1}}$ assuming that the voltammetric peak assignment was correct and that back reaction (27) is diffusion controlled. Thus, the observed rate constants are more than 10^3 times greater than the equilibrium data suggest is possible. Furthermore, it clearly is not justifiable to consider reaction (29) as being irreversible when the reverse reaction is expected to approach the diffusion controlled limit.

$$\mathrm{Th^{\cdot +} + Pyr \overset{K_{28}}{\rightleftarrows} Th^{\cdot} - Pyr^+} \qquad (28)$$

$$\mathrm{Th^{\cdot} - Pyr^+ + Th^{\cdot +} \xrightarrow{k_{29}} Th^+ - Pyr^+ + Th} \qquad (29)$$

$$\mathrm{Th^+ - Pyr^+ + H_2O \xrightarrow{fast} Th^+ - OH + PyrH^+} \qquad (30)$$

In our opinion it is ironic that work by Evans and Blount[11] which appears to have resulted in the postulation of a reaction mechanism for the hydroxylation of $\mathrm{Th^{\cdot +}}$ which is inconsistent with the experimentally derived rate law and in erroneous conclusions regarding the mechanism of hydroxylation in the presence of pyridine has been highly praised in recent review articles.[14,15] Hanson[14] states that this work[11] is an elegant demonstration of both the value of electrochemical techniques in the investigation of ion radicals and the subtleties of the reactivity of $\mathrm{Th^{\cdot +}}$. Shine[15] concludes that the complete and complex nature of the reaction was elucidated by Evans and Blount.[11]

The objective of the work described in this paper was to attempt to remove the uncertainties regarding the mechanism of the hydroxylation of $\mathrm{Th^{\cdot +}}$ in acetonitrile by carrying out experiments in buffered media in which the nature of the bases in proton transfer equilibria are better defined and to use kinetic isotope effects as a mechanistic probe. Preliminary results of this investigation have been reported.[16]

RESULTS

Kinetic measurements. The kinetics of the reactions of $\mathrm{Th^{\cdot +}}$ were studied by derivative cyclic voltammetry (DCV)[45] and the data were treated according to recently described procedures.[46] The analysis is based upon eqn. (31) which indicates a direct proportionality between the apparent rate

$$k_{\mathrm{app}} \sim v_{\frac{1}{2}}/C_{\mathrm{A}}^{z}C_{\mathrm{X}}^{x} \qquad (31)$$

constant k_{app} and $v_{\frac{1}{2}}$, the voltage sweep rate necessary for the derivative peak ratio to equal 0.500. The equation refers to reactions of intermediate B generated in reaction (32) and reacting by an unknown mechanism in which X is a reactant and

$$\mathrm{A} \pm \mathrm{e^-} \rightleftarrows \mathrm{B} \qquad (32)$$

assumes constant temperature.[46] In eqn. (31) C refers to concentrations, x to the reaction order in X and z is defined by eqn. (33) which gives the

Table 1. Derivative cyclic voltammetry kinetics of the hydroxylation of thianthrene cation radical in acetonitrile.[a]

Run	C_A/mM	C_X/M	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_X^4$	$v_{\frac{1}{2}}/C_X^3$
1	1.00	0.56	4.10	41.7	23.3
2	1.00	0.83	24.6	51.8	43.0
3	1.00	1.11	41.8	27.5	30.6
4	1.00	1.39	81.0	21.7	30.2
5	1.00	1.67	133.8	17.2	28.7
6	0.50	0.56	4.07	41.4	23.2
7	1.00	0.56	4.92	50.0	28.0
8	2.00	0.56	3.24	33.0	18.5
9	2.00	0.83	17.0	35.8	29.7
10	2.00	1.11	43.1	28.4	31.5
11	2.00	1.39	73.9	19.8	27.5
12	2.00	1.67	83.1	10.7	17.8

[a] C_A is the substrate concentration and C_X is the water concentration. All measurements were at 18.2 °C. $E_{sw} - E_{rev} = 300$ mV.

$$R_{A/B} = 1 + z \ (v_{\frac{1}{2}}/C_A^z = \text{constant}) \qquad (33)$$

combined reaction order in A and B ($R_{A/B}$) assuming only C_A is changed in the series of experiments used to determine $R_{A/B}$. For example, z is 0 for a first order reaction of B following charge transfer (32), 1 for a second order reaction of B, 0 when the reaction order in B is 2 and that for A is -1, *etc.*[46] Throughout this paper, A refers to Th, B to $Th^{\cdot +}$, and X to H_2O or D_2O.

Hydroxylation of $Th^{\cdot +}$ in neutral acetonitrile. The data summarized in Table 1 show the dependence of $v_{\frac{1}{2}}$ on C_A and C_X. The last two columns are tests for reaction orders of 4 and 3, respectively, in H_2O. It is clear from the data that the reaction order in water is dependent upon both C_A and C_X. An increasing trend in $v_{\frac{1}{2}}/C_X^x$ as C_X is increased is indicative that the value of x tested is too low. For example, the best fit for runs 1 and 2 is when x is equal to about 4.5. On the other hand for runs 3–5, $x = 3$ gives a constant value of $v_{\frac{1}{2}}/C_X^x$ which indicates that under these conditions the reaction is very nearly third order in water. At a higher value of C_A, data for runs 8–9 indicate that under these conditions x is very close to 4 but the data for runs 10–11 indicate that x is closer to 3. The best fit for the water concentration interval represented by runs 11–12 is for x close to 1. The reaction order in water is obviously a complex function of the reaction conditions.

Runs 6–8 show that $v_{\frac{1}{2}}$ increases in going from C_A equal to 0.5 to 1.0 mM but then declines upon a further doubling in C_A. This indicates that a value of $R_{A/B}$ cannot be assigned which gives a good fit of the data at all three concentrations, the value of z must be positive to be consistent with runs 6 and 7 and negative for runs 7 and 8.

A further complication was observed when DCV experiments were carried out at lower water concentrations. The data in Table 2 show the effect of v on the derivative peak ratio, R_I'. A well-behaved reaction gives data according to relationship (33).[47] In this case no such relationship was found and R_I' was observed to be a minimum at about 0.3 V/s

$$\ln R_I' = m \ln(1/v) + c \qquad (33)$$

Table 2. Evidence for the reversibility of the hydroxylation of thianthrene cation radical in acetonitrile.[a]

v/V s^{-1}	R_I'[b]
0.100	0.817 (0.004)
0.200	0.816 (0.004)
0.300	0.809 (0.003)
0.400	0.818 (0.004)
0.800	0.832 (0.007)
1.000	0.840 (0.005)
10.0	0.947 (0.010)

[a] Measurements on a 1.0 mM solution of thianthrene in the presence of water (278 mM) at 19.3 °C. $E_{sw} - E_{rev} = 300$ mV. [b] The ratio of first derivative peaks on the reverse and forward scans of a cyclic voltammogram. The numbers in parentheses refer to standard deviations in five measurements.

Table 3. Deuterium kinetic isotope studies of the reaction of thianthrene cation radical with water in acetonitrile.[a]

Run	X	C_X/M	$v_{\frac{1}{2}}$/V s^{-1}	k_H/k_D
13	H_2O	1.39	37.3	8.9
14	D_2O	1.39	4.2	
15	H_2O	2.09	91.8	9.5
16	D_2O	2.09	9.64	
17	H_2O	2.78	176.8	12.1
18	D_2O	2.78	14.6	

[a] Measurements at 19.4 °C. $E_{sw} - E_{rev}$ = 200 mV. C_A = 1.0 mM.

and to increase with further decreases in v. A similar phenomenon was observed in related studies and found to be due to an overall reversible reaction.[48] This implies that reaction (1) is reversible under the reaction conditions.

The data in Table 3 show that the hydroxylation of $Th^{\cdot +}$ in neutral acetonitrile is subject to an appreciable deuterium kinetic isotope effect ranging from 8.9 at C_X equal to 1.39 M to 12.1 at a water concentration of 2.78 M.

Measurements at a water concentration of 1.39 M resulted in data which gave a constant value of $v_{\frac{1}{2}}/C_A^z$ with $z = 0.3$ while in the presence of D_2O (2.78 M) the relationship was satisfied with $z = 0.6$ as shown in Table 4. These data indicate that the reaction order in cation radical is greater than 1 and that the reaction is probably inhibited by Th.

Hydroxylation of $Th^{\cdot +}$ in acetonitrile containing TFA. Data from runs 24 – 26 (Table 5) show that the reaction order in water in this medium follows the same general pattern as in neutral acetonitrile. Runs 24 and 25 give data consistent with $x = 4$ while that for runs 25 and 26 taken together is more consistent with $x = 3$. Thus, it appears that the reaction order in water is a continually changing function depending strongly on C_X. Comparing $v_{\frac{1}{2}}$ for runs 24 – 26 with those for runs 1, 3 and 5 (Table 1) results in the conclusion that TFA at a concentration of 9.9 mM has very little effect on the apparent rate of the reaction. The concentration of TFA was successively doubled in runs 26 to 29 with the result that about a 10 % decrease in the apparent rate constant was observed with each concentration change.

Hydroxylation of $Th^{\cdot +}$ in acetonitrile containing 2,6-lutidine. The data in Table 6 show that in the presence of 2,6-lutidine (L) (2.2 mM) and water (1.11 M) the apparent rate constant decreases significantly with increases in C_A. When $z = -0.6$,

Table 4. Reaction order analysis of the reaction of the thianthrene cation radical with water in acetonitrile.[a]

Run	X	C_X/M	C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_A^{0.3}$	$v_{\frac{1}{2}}/C_A^{0.6}$
19	H_2O	1.39	0.50	28.9	283	–
20	H_2O	1.39	1.00	38.1	303	–
21	H_2O	1.39	2.00	45.1	291	–
22	D_2O	2.78	1.00	14.6	–	921
23	D_2O	2.78	2.00	22.9	–	953

[a] Measurements at 19.4 °C. $E_{sw} - E_{rev}$ = 200 mV.

Table 5. The effect of trifluoroacetic acid on the kinetics of the hydroxylation of thianthrene cation radical in acetonitrile.[a]

Run	C_{TFA}/mM	C_X/M	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_X^4$	$v_{\frac{1}{2}}/C_X^3$
24	9.9	0.56	3.54	36.0	20.2
25	9.9	1.11	51.0	33.6	37.3
26	9.9	1.67	150.4	19.3	32.3
27	19.8	1.67	123.3	–	–
28	39.6	1.67	111.8	–	–
29	79.2	1.67	96.7	–	–

[a] Substrate concentration was 1.00 mM and the temperature was 18.2 °C. $E_{sw} - E_{rev}$ = 300 mV.

Table 6. Reaction order analysis for the hydroxylation of thianthrene cation radical in acetonitrile containing 2,6-lutidine.[a]

Run	C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_A^{-0.6}$
30	0.25	20.2	0.139
31	0.50	14.0	0.146
32	1.00	9.13	0.145

[a] In solvent containing water (1.11 M) and 2,6-lutidine (2.2 mM) at 18.2 °C. $E_{sw} - E_{rev} = 300$ mV.

Table 7. The reaction order in water during hydroxylation of thianthrene cation radical in acetonitrile containing 2,6-lutidine.[a]

Run	C_L/mM	C_X/M	$v_{\frac{1}{2}}$/V s^{-1}	$v_{\frac{1}{2}}/C_X$
33	10.8	0.28	7.71	27.5
34	10.8	0.56	7.91	14.1
35	10.8	1.11	13.5	12.2
36	2.2	0.28	4.69	16.8
37	2.2	0.56	6.67	11.9
38	2.2	0.83	9.70	11.7
39	2.2	1.11	13.6	12.3
40	2.2	1.67	21.7	13.0

[a] Substrate concentration was 0.50 mM and the measurements were at 18.2 °C. $E_{sw} - E_{rev} = 300$ mV.

$v_{\frac{1}{2}}/C_A^z$ was very nearly constant. A comparison of the data for run 32 with that for run 3 (Table 1) shows that $v_{\frac{1}{2}}$ is about a factor of 4 lower in the presence of L. With the exception of that from run 33 the data in Table 7 show that the reaction order in water is very nearly 1 in the presence of L either at a concentration of 2.2 or 10.8 mM.

Hydroxylation of Th$^{\cdot +}$ in buffered acetonitrile. Runs 41 – 43 demonstrate the effect of substrate concentration on the apparent rate constant for reactions carried out in a buffer solution consisting of $LH^+CF_3CO_2^-$ (3.3 mM) and L (7.5 mM) in solvent containing water (1.11 M). The best data fit was obtained for $v_{\frac{1}{2}}/C_A^z$ when $z = 0.75$ (Table 8). In buffer solution containing excess TFA, $v_{\frac{1}{2}}/C_{CF_3CO_2^-}$ was observed to be constant indicating a reaction order of 1 in the anion (Table 9). The data in Table 10 show that either in the presence of H_2O or D_2O $v_{\frac{1}{2}}$ increases nearly linearly with increasing $CF_3CO_2^-$ concentration in buffer with excess L present but decreases when excess TFA is present. A kinetic isotope effect of the order of 2 was observed in the basic buffer (runs 48 – 51).

The data in Table 11 show the effect on k_H/k_D of successive additions of L to a solution containing TFA originally present at a concentration of 21.8 mM. Before adding L, k_H/k_D was observed to be equal to 3.5 and approached 1 as the concentration of $LH^+CF_3CO_2^-$ was increased by addition of L.

The effect of substrate concentration on the apparent rate constants and the deuterium kinetic isotope effect is demonstrated by the data in Table 12. In the presence of either nucleophile $v_{\frac{1}{2}}/C_A^z$ was very nearly constant when z was 0.83 indicating an apparent value of $R_{A/B}$ of about 1.83. In all cases, the value of k_H/k_D was only slightly greater than 1.

Voltammetric study of the hydroxylation of Th$^{\cdot +}$ in acetonitrile in the presence of pyridine and TFAn. A cyclic voltammogram for the oxidation of Th in acetonitrile containing Bu_4NBF_4 (0.2 M) at a voltage sweep rate of 100 mV/s measured in the

Table 9. The reaction order in trifluoroacetate ion under pseudo second order reaction conditions.[a]

Run	C_L/mM	$v_{\frac{1}{2}}$/V s^{-1}	$(v_{\frac{1}{2}}/C_L) \times 10^{-3}$
44	1.7	16.2	9.53
45	3.4	28.8	8.47
46	5.1	43.9	8.61
47	6.8	62.0	9.12

[a] In solvent containing H_2O (1.11 M) and trifluoroacetic acid (16.3 mM) at 19.4 °C. $E_{sw} - E_{rev} = 200$ mV.

Table 8. Reaction order analysis of the hydroxylation of thianthrene cation radical in buffered acetonitrile.[a]

Run	C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	$(v_{\frac{1}{2}}/C_A) \times 10^{-3}$	$(v_{\frac{1}{2}}/C_A^{0.75}) \times 10^{-3}$
41	0.25	12.5	50.0	6.29
42	0.50	21.3	42.6	6.37
43	1.00	33.6	33.6	5.98

[a] In solvent containing water (1.11 M), 2,6-lutidine (10.8 mM) and trifluoroacetic acid (3.3 mM) at 18.6 °C. $E_{sw} - E_{rev} = 200$ mV.

Table 10. Kinetic evidence for the catalysis of the hydroxylation of thianthrene cation radical by trifluoroacetate ion.[a]

Run	X[b]	C_{TFA}/mM	$v_{\frac{1}{2}}$/V s^{-1}	$(v_{\frac{1}{2}}/C_{TFA})\times 10^{-3}$	k_H/k_D
48	H_2O	3.3	83.6	25.3	2.0
49	D_2O	3.3	41.7	12.6	
50	H_2O	6.6	134.4	20.4	2.3
51	D_2O	6.6	58.5	8.9	
52	D_2O	9.9	81.4	8.2	
53	D_2O	13.2	79.2	6.0	
54	D_2O	16.5	67.3	4.1	

[a] In solvent containing 2,6-lutidine (10.8 mM) and thianthrene (0.5 mM). $E_{sw}-E_{rev}=200$ mV. Measurements at 19.4 °C. [b] At a concentration of 1.11 M.

Table 11. Effect of trifluoroacetate ion on the magnitude of the deuterium kinetic isotope effect.[a]

Run	*X*[b]	C_L/mM	$v_{\frac{1}{2}}$/V s^{-1}	k_H/k_D
55	H_2O	0	20.0	3.5
56	D_2O	0	5.64	
57	H_2O	1.15	47.6	1.7
58	D_2O	1.15	28.0	
59	H_2O	2.3	77.9	1.3
60	D_2O	2.3	58.2	
61	H_2O	4.6	150	1.2
62	D_2O	4.6	125	

[a] In solvent containing trifluoroacetic acid (21.8 mM) and thianthrene (0.5 mM) at 19.4 °C. $E_{sw}-E_{rev}=200$ mV. [b] At a concentration of 1.11 M.

presence of Al_2O_3 is illustrated in Fig. 1a. The voltammogram measured under the same conditions after the addition of pyridine (50 mM) is shown in Fig. 1b. The effect of the addition of pyridine was to bring about an approximate doubling of the oxidation peak current and the complete elimination of current for the reverse process. This behaviour is typical for a rapid ECE type process. The voltammogram illustrated in Fig. 1c is for the same solution after the addition of TFAn (6%). The oxidation peak current in this case was nearly identical to that in 1b but the process appears as a quasi-reversible charge transfer indicating complete chemical reversibility of the processes taking place.

DISCUSSION

Kinetic data for the hydroxylation of thianthrene cation radical are now available under a wide variety of conditions; (i) in acetonitrile or dichloromethane as solvent, (ii) in the presence of trifluoroacetic acid, (iii) in the presence of pyridine and 2,6-lutidine, (iv) in acidic acetonitrile buffers and (v) in basic acetonitrile buffers. Thus, it is not satisfactory to demonstrate a mechanism consistent with data obtained only under one set of experimental conditions. It is highly desirable to

Table 12. A kinetic isotope effect study under pseudo second order reaction conditions.[a]

Run	X[b]	C_A/mM	$v_{\frac{1}{2}}$/V s^{-1}	$(v_{\frac{1}{2}}/C_A^{0.83})\times 10^{-4}$	k_H/k_D
63	H_2O	0.25	32.5	3.17	1.03
64	D_2O	0.25	31.4	3.07	
65	H_2O	0.50	(70.0)	(3.84)	1.17
66	D_2O	0.50	59.6	3.27	
67	H_2O	1.00	102.9	3.18	1.02
68	D_2O	1.00	101.0	3.12	

[a] In solvent containing trifluoroacetic acid (16.3 mM) and 2,6-lutidine (3.4 mM) at 19.4 °C. $E_{sw}-E_{rev}=200$ mV. [b] At a concentration of 1.11 M.

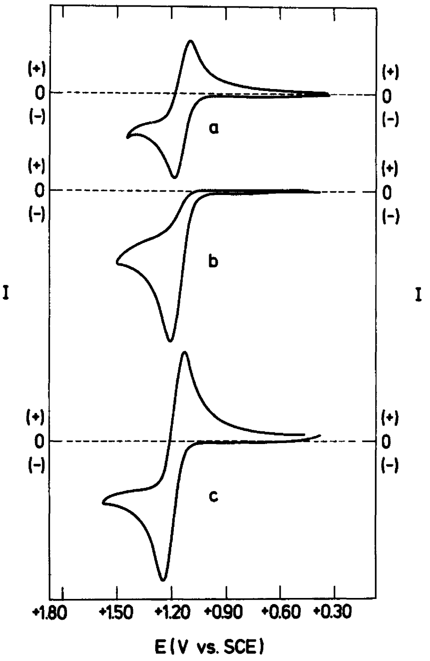


Fig. 1. Cyclic voltammograms of thianthrene in acetonitrile containing Bu_4NBF_4 (0.2 M). a, In the presence of neutral Al_2O_3, b, Solution a plus pyridine (50 mM) and c, Solution b plus TFAn (6 %). Sweep-rate: 100 mV s^{-1}, $t = 22$ °C.

have a mechanistic framework unifying the results from all of the diverse experiments.

The most pertinent results that require explanation are the following: (1) The reaction order in water for reactions conducted in either neutral acetonitrile or in the presence of TFA is varying in the range of 2 – 5 and strongly depends upon the reaction conditions. (2) The reaction order in water is very close to 1 in acetonitrile containing 2,6-lutidine. (3) The reaction order in water is 1 for reactions carried out in CH_2Cl_2 – TFA.[12] (4) The apparent second order rate constant in acetonitrile is inversely proportional to the concentration of strong mineral acid[11] but only slightly affected by TFA. (5) The deuterium kinetic isotope effect for reactions of $Th^{\cdot+}$ with H_2O or D_2O varies from greater than 10 to about 1 and can be related to the reaction order, $R_{A/B}$.[16] (6) In the presence of pyridine and TFAn, cyclic voltammetry shows that Th is involved in a $2e^-$ oxidation process of the ECE type that is chemically reversible, *i.e.* the CV peak current ratio is approximately unity, in contrast to earlier results which indicated rapid and irreversible hydroxylations under the same conditions.[11]

In order to explain the high reaction orders in water when the reaction is carried out in neutral acetonitrile or in the presence of TFA it is tempting to postulate a series of hydration equilibria (34) – (36) which could explain why the reaction order is higher at low water concentrations. A certain degree

$$Th^{\cdot+} + H_2O \overset{K_{34}}{\rightleftarrows} Th^{\cdot+}(H_2O) \quad (34)$$

$$Th^{\cdot+}(H_2O) + H_2O \overset{K_{35}}{\rightleftarrows} Th^{\cdot+}(H_2O)_2 \quad (35)$$

$$Th^{\cdot+} + n\,H_2O \overset{K_{36}}{\rightleftarrows} Th^{\cdot+}(H_2O)_n \quad (36)$$

of hydration, for example a hydration number n as in eqn. (36), might be necessary before bond formation (37) takes place. If the magnitude of the hydration equilibrium constants were such that as

$$Th^{\cdot+}(H_2O)_n \rightleftarrows Th^{\cdot}-OH + H_3O^+ + (n-2)\,H_2O \quad (37)$$

the water concentration is increased the equilibria, one at a time, would be displaced to the right and the reaction order in water could conceivably be n at low concentration when all equilibria are displaced to the left and then decrease by one unit at a time until all equilibria lie to the right and the rate would become independent of $[H_2O]$. The data in Tables 1 – 5 could be incorporated into a mechanism involving the hydration equilibria. However, the hydration equilibria explanation is doomed by the data in Table 7. The presence of 2,6-lutidine in concentrations as low as 2.2 mM has a profound influence on the water reaction order. Under these conditions, the hydroxylation of $Th^{\cdot+}$ is clearly first order in H_2O. It is inconceivable that the low concentrations of 2,6-lutidine could completely inhibit the hydration equilibria (34) – (36).

The effect of the base, 2,6-lutidine, on the reaction kinetics suggests that the complexity of the water reaction order is simply a consequence of acid – base equilibria. In general terms, where the nature of bases B are not specified, the mechanism of the hydroxylation can be formulated as in eqns. (38) – (41). When B is water, for every mol of ThO

$$Th^{\cdot+} + H_2O \overset{K_{38}}{\rightleftarrows} Th^{\cdot}-\overset{+}{O}H_2 \quad (38)$$

$$Th^{\cdot}-\overset{+}{O}H_2 + B \overset{K_{39}}{\rightleftarrows} Th^{\cdot}-OH + BH^+ \quad (39)$$

$$Th^{\cdot}-OH+Th^{\cdot +}\underset{k_{-40}}{\overset{k_{40}}{\rightleftharpoons}}Th^{+}-OH+Th \qquad (40)$$

$$Th^{+}-OH+B\xrightarrow{k_{41}}ThO+BH^{+} \qquad (41)$$

produced, two mol of H_3O^+ are formed which can show their inhibiting influence *via* reaction (39). Under conditions where electron transfer reaction (40) is rate determining[11] a reaction order of 2 in water is predicted by this mechanism in the absence of other complications. However, the observed order is higher and in this work we have shown that it is varying as well. The higher order can be accounted for by equilibrium (42) if we assume that H_3O^+ is a more effective participant

$$H_3O^{+}+n\,H_2O\overset{K_{42}}{\rightleftharpoons}H_3O^{+}(H_2O)_n \qquad (42)$$

in reverse reaction (39) than is $H_3O^+(H_2O)_n$.

Mechanism (38)–(41) accounts for the fact that the reaction order in water is 1 in the presence of 2,6-lutidine. In this case B/BH^+ is L/LH^+ and the only participation of water in the hydroxylation is as the nucleophile in reaction (38). Equilibrium (42) is insignificant under these conditions due to very low H_3O^+ concentrations.

The fact that TFA only very slightly inhibits the rate of hydroxylation of $Th^{\cdot +}$ (Table 5) is indicative that equilibrium (43) is displaced to the left and significant concentrations of H_3O^+ do not

$$TFA+H_2O\overset{K_{43}}{\rightleftharpoons}CF_3CO_2^{-}+H_3O^{+} \qquad (43)$$

result from the presence of TFA in the solvent system. On the other hand, strong mineral acids do inhibit the reaction and this must be due to H_3O^+ when they are present.

Mechanism (38)–(41) does not provide an explanation of the kinetics of the hydroxylation in CH_2Cl_2-TFA.[12] The most compelling evidence that a different mechanism is involved in the latter solvent system is that the reaction is first order in H_2O. Water must be the strongest base in this solvent and steps (38) and (39) require that the minimum reaction order in H_2O is 2 providing that K_{38} and K_{39} are small. Furthermore, if equilibrium (42) is responsible for the high reaction orders in acetonitrile it would be expected to be as, if not more, important in CH_2Cl_2-TFA.

We have proposed that the mechanism of hydroxylation of $Th^{\cdot +}$ in CH_2Cl_2 is the complexation sequence (44)–(46).[12] As pointed out in the previous paragraph, the mechanism is different in the two solvents, acetonitrile and dichloromethane. The difference in mechanism is readily accounted for

$$Th^{\cdot +}+H_2O\overset{K_{44}}{\rightleftharpoons}(Th/H_2O)^{\cdot +} \qquad (44)$$

$$(Th/H_2O)^{\cdot +}+Th^{\cdot +}\underset{k_{-45}}{\overset{k_{45}}{\rightleftharpoons}}(Th/H_2O)^{2+}+Th \qquad (45)$$

$$(Th/H_2O)^{2+}\xrightarrow{k_{46}}Th^{+}-\overset{+}{O}H_2 \qquad (46)$$

by considering the expected effect of solvent polarity on equilibrium (38). Forward reaction (38) involves the formation of a covalent bond between S and O accompanied by the concentration of charge on the oxygen atom. Since the charge is dispersed in $Th^{\cdot +}$, K_{38} is expected to be strongly solvent dependent and greater the more polar the solvent. Thus, in non-polar CH_2Cl_2, equilibrium (38) may be insignificant compared to (44). Since reaction (44) is simply the formation of a complex it is likely that it precedes equilibrium (38) in the more polar solvent acetonitrile as well. In dichloromethane reactions (45) and (46) can take place leading eventually to ThO. In order for mechanism (44)–(46) to be favourable, $(Th/H_2O)^{\cdot +}$ must be significantly more easily oxidized than $Th^{\cdot +}$ so that the magnitude of K_{45} is appreciably greater than K_2 in this solvent system. The effect of complex formation is expected to be in that direction since charge repulsion in the dication is partially relieved. A related phenomenon is observed for disproportionation equilibria of anion radicals which are profoundly affected by association of dianions with counter ions.[49]

Since TFA does not inhibit the hydroxylation of $Th^{\cdot +}$ in acetonitrile, we concluded that K_{43} is not of sufficient magnitude for equilibrium (43) to produce significant concentrations of H_3O^+. The effect of solvent polarity on equilibrium (43) is expected to be a displacement to the left as the solvent becomes less polar. On this basis we must conclude that equilibrium (43) is even less important in CH_2Cl_2 than in acetonitrile.

The inhibition of the hydroxylation by TFA in dichloromethane is difficult to explain in quantitative terms. The effect of TFA could either be the deactivation of water or the stabilization of $Th^{\cdot +}$ by specific solvation. In this respect it is informative to recall that reversible cyclic voltammograms have been reported in H_2O-TFA (50 vol.-%). In this system there is a very high mol fraction of water and the role of TFA is not likely to be deactivation of water.[19]

In neutral acetonitrile a large deuterium kinetic isotope effect ($k_H/k_D = 9-12$) was observed (Table 3) under conditions where $R_{A/B}$ was about 1.3 in the presence of H_2O and 1.6 in the presence of D_2O (Table 4). Three rate laws consistent with mechanism (38)–(41) have been shown to be of importance depending upon the relative magnitude of k_{40}, k_{-40} and k_{41}.[16] The rate laws (47)–(49) must be consistent with the observed reaction orders as well

$$\text{Rate} = 2\, k_{41}K_{38}K_{39}K_{40}[\text{Th}^{\cdot+}]^2[\text{H}_2\text{O}][\text{B}]^2/[\text{BH}^+][\text{Th}] \quad (47)$$

$$\text{Rate} = 2\, k_{40}K_{38}K_{39}[\text{Th}^{\cdot+}]^2[\text{H}_2\text{O}][\text{B}]/[\text{BH}^+] \quad (48)$$

$$\text{Rate} = 2\, k_{40}k_{41}K_{38}K_{39}[\text{Th}^{\cdot+}]^2[\text{H}_2\text{O}][\text{B}]^2/[\text{BH}^+](k_{41}[\text{B}] + k_{-40}[\text{Th}]) \quad (49)$$

as the kinetic isotope effects. In neutral or acidic acetonitrile B is most likely water. The large value of k_H/k_D suggests that proton transfers (39) and (41) both contribute to the rate and rate law (49) provides for the non-integral reaction orders. When the nucleophile is H_2O, $R_{A/B}$ is about 1.3 which indicates that the limiting case where reaction (40) can be considered to be in equilibrium and $R_{A/B}$ is 1 is approached. In acidic buffer (Table 12) $R_{A/B}$ was observed to be equal to 1.83 which indicates that this case approximates the condition where the electron transfer reaction (40) is rate determining and that rate law (48) applies. A low value of k_H/k_D was observed in this case, 1.08 ± 0.08. This is also consistent with rate law (48) since in this case the proton transfer takes place in an equilibrium step (39).[50] In basic buffer (Table 8) $R_{A/B}$ is about 1.7 which indicates that the rates of back reaction (40) and reaction (41) are of comparable magnitude and that rate law (49) is approximated by the data measured under these conditions. In this case k_H/k_D is intermediate in value and equal to about 2.2 (Table 10). The observed kinetic isotope effect is once again consistent with the reaction orders and rate law (49) and arises from proton transfer step (41).

It is of interest to observe the effect of trifluoroacetate ion on k_H/k_D in acidic buffer (Table 11). In the absence of $CF_3CO_2^-LH^+$ the observed value was 3.5. As the concentration of the anion is increased k_H/k_D decreases and approaches a value consistent with only an equilibrium isotope effect. This implies that the rate of reaction (41) increases with increasing trifluoroacetate ion and at concentrations of between about 2.3 and 4.6 mM becomes great enough so that it no longer contributes to controlling the rate of the overall reaction. Under conditions where rate law (48) apply (Table 9) the reaction is first order in trifluoroacetate ion. This implies that $CF_3CO_2^-$ is the only base participating in equilibrium (39).

Reactions carried out in the presence of 2,6-lutidine (Tables 6 and 7) are significantly slower than those in either neutral or acidic buffer. The reason for this is apparent from the data in Table 6. Under these conditions $R_{A/B}$ is of the order of 0.4 which indicates that an inhibitor is formed during the reaction. This implies that LH^+ participates in back reaction (39). However, when both 2,6-lutidine and $CF_3CO_2^-LH^+$ are present, $R_{A/B}$ is of the order of 1.75. This means that trifluoroacetate is a more effective base in reaction (39) than is L. It is possible that there is some inhibition by LH^+ in this case as well.

The cyclic voltammograms (Fig. 1) measured for the oxidation of Th in the presence of pyridine indicate that reactions (28) to (30) are fast and irreversible when water is present. When water is effectively removed by reaction with TFAn (25) and the TFA effectively removed by having neutral alumina present in the cell only reactions (28) and (29) take place and are reversible. This clearly shows that the oxidation peak attributed to $\text{Th}^{\cdot}-\text{Pyr}^+$ by Evans and Blount[11] was due to some other process. Apparently under the conditions of their work there was no pyridine present due to protonation by TFA. The peak potential for reaction (50) is slightly positive for the reversible

$$\text{Th} + \text{Pyr} \xrightleftharpoons{E_{50}} \text{Th}^+ - \text{Pyr}^+ + 2\,\text{e}^- \quad (50)$$

one electron oxidation of Th (8). This implies that the reversible potential for reaction (26) is somewhat but not very much more positive than E_{50} since the latter would fall half-way in between that for the two one electron redox processes. Thus, we can make a reliable estimate of K_{27} to be of the order of 10^{-1}, *i.e.* the interpretation by Evans and Blount[11] of the voltammogram for the oxidation of Th in the presence of pyridine and TFAn led to an error of about 10^6 in K_{27}. Therefore, the mechanism for the hydroxylation of $\text{Th}^{\cdot+}$ in the presence of pyridine proposed by Evans and

Blount[11] requires modification. It is very likely that the kinetic data described in Table II of Ref. 11 refer to the hydroxylation of $Th^{\cdot +}$ in the presence of $CF_3CO_2^-$ $PyrH^+$ and that data are not available for the reaction in the presence of pyridine. Our determination of K_{27} to be 10^{-1} calls for reaction (27) to be very rapid and would be expected to be in equilibrium so that we predict that the reaction follows rate law (51).

$$\text{Rate} = 2\,k_{30}K_{27}K_{28}[Th^{\cdot +}]^2[Pyr][H_2O]/[Th] \qquad (51)$$

We have observed quasi-reversible cyclic voltammograms for the oxidation of Th in the presence of $CF_3CO_2^-$ and TFAn, conditions where essentially no water is present, and find that the overall two electron process to give voltammograms very nearly identical to Fig. 1c. This indicates that reaction (52) is reversible under these conditions. This then

$$Th + CF_3CO_2^- \rightleftarrows Th^+ - OCOCF_3 + 2\,e^- \qquad (52)$$

suggests that the mechanism of the hydroxylation of $Th^{\cdot +}$ in the buffers could be described by reactions (53)–(56) and rate law (57). One fact that argues

$$Th^{\cdot +} + CF_3CO_2^- \xrightleftharpoons{K_{53}} Th^{\cdot} - OCOCF_3 \qquad (53)$$

$$Th^{\cdot} - OCOCF_3 + Th^{\cdot +} \xrightleftharpoons{K_{54}} Th^+ - OCOCF_3 + Th \qquad (54)$$

$$Th^+ - OCOCF_3 + H_2O \xrightleftharpoons[k_{-55}]{k_{55}} Th^+ - OH + TFA \qquad (55)$$

$$Th^+ - OH + CF_3CO_2^- \xrightarrow{k_{56}} ThO + TFA \qquad (56)$$

$$\text{Rate} = 2\,k_{56}K_{53}K_{54}K_{55}[Th^{\cdot +}]^2[CF_3CO_2^-]^2 [H_2O]/[Th][TFA] \qquad (57)$$

strongly against this mechanism is that under conditions where electron transfer reaction (54) is rate determining there is no possibility of a deuterium kinetic isotope effect. It therefore appears unlikely that nucleophilic attack by trifluoroacetate (53) significantly contributes to the rate of hydroxylation of $Th^{\cdot +}$.

In conclusion, we point out that in order to establish a mechanism for a reaction as complicated as the hydroxylation of thianthrene cation radical, it is necessary to obtain experimental evidence of various types over a wide range of reaction conditions. In this case, the kinetic isotope effect data was an indispensible aid in the interpretation of kinetic results.

EXPERIMENTAL

The instrumentation, electrodes, cells, data handling procedures and solvent and supporting electrolyte purification were the same as described recently.[51] Thianthrene (Fluka, *purum*), trifluoroacetic acid (Fluka, *purum*), trifluoroacetic anhydride (Fluka, *purum*) and 2,6-lutidine (Fluka, *purum*) were used as received.

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