(1.17 L) was shaken in a Parr hydrogenator at 40 psi for 17.5 h. The reaction mixture was filtered through sulka floc, and the solid was rinsed with absolute EtOH (2 × 15 mL). The reaction mixture was concentrated, and the resultant solid was dissolved in water (1.4 L). The aqueous solution was basified to pH 9 with 10% aqueous NaOH. The precipitate was collected by suction filtration and washed with water (2 × 100 mL). The solid was recrystallized in 1:1 EtOH–water to provide **32** as amber needles (9.57 g, 76%). A small portion of this latter solid was recrystallized from 1:1 petroleum ether–CH_2Cl_2: mp 214–216 °C; NMR (DMSO-d_6, 200 MHz) δ 4.02 (s, 3 H, ArOC*H*$_3$), 4.46 (s, 2 H, NC*H*$_2$), 7.80 (t, 2 H, *J* = 8.8 Hz, Ar*H*), 8.26 (d, 1 H, *J* = 9.0 Hz, Ar*H*), 8.78 (s, 1 H, N*H*), 9.48 (d, 1 H, *J* = 9.1 Hz, Ar*H*); IR (KBr) 3190 and 3080 (NH), 1676 (C=O); MS (*m/e*) 281 (100), 253 (76), 212 (33). Anal. ($C_{14}H_{10}F_3NO_2$) C, H, N.

2,3-Dihydro-6-(trifluoromethyl)-7-methoxy-1-oxo-1*H*-benz[*e*]isoindole-2-acetic Acid Methyl Ester (41). Compound **41** was prepared from **32** using the conditions described for **19** (yield 46%): mp 190–192 °C (2:1 hexane–$CHCl_3$); NMR ($CDCl_3$, 200 MHz) δ 3.76 (s, 3 H, CO_2CH_3), 4.02 (s, 3 H, ArOC*H*$_3$), 4.46 (s, 2 H, NC*H*$_2$), 4.57 (s, 2 H, NC*H*$_2$CO$_2$), 7.48 (d, 1 H, *J* = 9.5 Hz, Ar*H*), 7.60 (d, 1 H, *J* = 9.3 Hz, Ar*H*), 8.42 (d, 1 H, *J* = 9.3 Hz, Ar*H*), 9.49 (d, 1 H, *J* = 9.5 Hz, Ar*H*); IR ($CHCl_3$) 1748 (C=O), 1681 (C=O), 1602 (C=O). Anal. ($C_{17}H_{14}F_3NO_4$) C, H, N.

2,3-Dihydro-6-(trifluoromethyl)-7-methoxy-1-thioxo-1*H*-benz[*e*]isoindole-2-acetic Acid Methyl Ester (42). Lawesson's reagent (5.37 g, 13.32 mmol) was added to a stirred suspension of lactam **41** (3.91 g, 11.1 mmol) in toluene (40 mL) at room temperature under a dry N_2 atmosphere. The reaction was heated at reflux for 2.5 H, and the cooled reaction mixture was diluted with EtOAC (100 mL), preabsorbed onto silica gel, and flash chromatographed (7:3 to 3:7 petroleum ether–EtOAc, gradient elution, silica) to prioride **42** as a beige solid (2.44 g, 60%): mp 187–188.5 °C (2:1 $CHCl_3$–petroleum ether); NMR ($CDCl_3$, 200 MHz) δ 3.79 (s, 3 H, CO_2CH_3), 4.02 (s, 3 H, ArOC*H*$_3$), 4.93 (s, 2 H, NC*H*$_2$), 5.04 (s, 2 H, NC*H*$_2$CO$_2$), 7.39 (d, 1 H, *J* = 9.4 Hz, Ar*H*), 7.92 (d, 1 H, *J* = 9.3 Hz, Ar*H*), 8.08 (d, 1 H, *J* = 9.2 Hz, Ar*H*), 8.29 (d, 1 H, *J* = 9.6 Hz, Ar*H*); IR ($CHCl_3$) 2990 and 2960 (CH), 1746 (C=O), 1622 (C=C); MS (*m/e*) 369 (99), 337 (11), 310 (58), 309 (100), 282 (68). Anal. ($C_{17}H_{14}F_3NO_3S$) C, H, N.

2,3-Dihydro-6-(trifluoromethyl)-7-methoxy-1-oxo-1*H*-benz[*e*]isoindole-2-acetic Acid (6a). Compound **6a** was prepared from **41** using the conditions described for **5d** (yield 48%): mp 264–265 °C (2:1 EtOH–water); NMR (DMSO-d_6, 400 MHz) δ 4.03 (s, 3 H, ArOC*H*$_3$), 4.36 (s, 2 H, NC*H*$_2$), 4.61 (s, 2 H, C*H*$_2$CO$_2$), 7.82 (d, 1 H, *J* = 9.5 Hz, Ar*H*), 7.86 (d, 1 H, *J* = 9.0 Hz, Ar*H*), 8.29 (d, 1 H, *J* = 7.8 Hz, Ar*H*), 9.42 (d, 1 H, *J* = 9.4 Hz, Ar*H*); IR (KBr) 1735 (C=O), 1651 (C=O); MS (*m/e*) 339 (56), 294 (100), 266 (36), 251 (27), 239 (29). Anal. ($C_{16}H_{12}F_3NO_4$) C, H, N.

2,3-Dihydro-6-(trifluoromethyl)-7-methoxy-1-thioxo-1*H*-benz[*e*]isoindole-2-acetic Acid (6b). A suspension of **42** (2.08 g, 5.63 mmol) in 6 N HCl (80 mL) was heated at reflux for 15 h, with more 6 N HCl (40 mL) added after 3 h. The reaction was cooled to room temperature and diluted with water (100 mL). The acidic suspension was filtered, and the solid was washed with water (2 × 30 mL) and triturated with 1:1 EtOAc–petroleum ether (2 × 40 mL). Recrystallization (EtOAc) provided **6b** as a light yellow solid (0.50 g, 25%): mp 253–255.5 °C dec; NMR (DMSO-d_6, 400 MHz) δ 4.05 (s, 3 H, ArOC*H*$_3$), 4.86 (s, 2 H, NC*H*$_2$), 5.30 (s, 2 H, NC*H*$_2$CO$_2$), 7.78 (d, 1 H, *J* = 9.3 Hz, Ar*H*), 7.99 (d, 1 H, *J* = 9.1 Hz, Ar*H*), 8.20 (d, 1 H, *J* = 7.7 Hz, Ar*H*), 8.36 (d, 1 H, *J* = 9.3 Hz, Ar*H*); IR (KBr) 1722 (C=O); MS (*m/e*) 355 (100), 310 (45), 309 (78), 296 (24), 282 (77). Anal. ($C_{16}H_{12}F_3NO_3S$) C, H, N.

Acknowledgment. We are grateful to the Analytical Department of Wyeth-Ayerst for elemental analyses and 400-MHz ^1H NMR, ^{13}C NMR, and mass spectroscopy data and to Dr. Jane Millen for testing the compounds in the bovine lens aldose reductase screen. We also thank Professors D. Curran (University of Pittsburg) and S. Burke (University of Wisconsin) for helpful discussions.

Evidence for Electron Transfer in Reactions of Thianthrene Cation Radical with Dialkylmercurials

Stanislaw Lochynski,[1] Henry J. Shine,* Miroslaw Soroka, and T. Krishnan Venkatachalam

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

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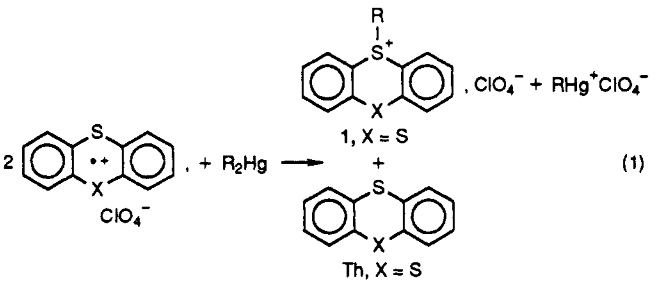
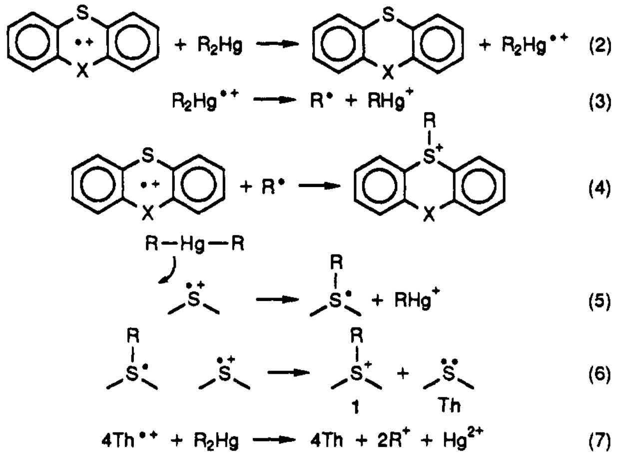
Reactions of dialkylmercurials (R_2Hg) with thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) in acetonitrile solution have been studied in quantitative detail. Evidence was obtained from reactions of MeHgR (R = Et, *i*-Pr, *t*-Bu) that reaction begins with electron transfer rather than with electrophilic cleavage of an alkyl–mercury bond. That is, each reaction gave $MeHg^+$ and $R^\bullet$, diagnostic of the formation and decomposition of $MeHgR^{\bullet+}$, rather than 5-methylthianthreniumyl perchlorate (**1a**), which would have been diagnostic of electrophilic displacement of the least hindered group (Me). The radicals $R^\bullet$ either were trapped at the sulfur atom of $Th^{\bullet+}$ to form a 5-alkylthianthreniumyl perchlorate ($Et^\bullet$, **1b**) and at the ring positions of $Th^{\bullet+}$ to form 1- and 2-alkylthianthrenes and dialkylthianthrenes ($Et^\bullet$, *i*-$Pr^\bullet$) or were oxidized to the cations R^+ ($Et^\bullet$, *i*-$Pr^\bullet$, and *t*-$Bu^\bullet$). Products of R^+ were then obtained, after workup with 4 M aqueous LiCl, as alkene, ROH, $RNHCOCH_3$, and RCl. These reactions had the stoichiometric ratio of reactants $2Th^{\bullet+}ClO_4^-$/MeHgR. Reactions of symmetrical R_2Hg sometimes followed this stoichiometry (R = Me, Et, Bu) and led to RHg^+ and 5-R-thianthreniumyl perchlorates (**1a**,**b**,**e**). Other R_2Hg (R = *t*-Bu, benzyl, allyl) underwent oxidation by 4 equiv of $Th^{\bullet+}ClO_4^-$. Di-*tert*-butyl- and dibenzylmercury gave products derived entirely from the respective cation, R^+. Diallylmercury gave some of the sulfonium product, 5-allylthianthreniumyl perchlorate (**1g**). None of the reactions with R = *i*-Pr, *t*-Br, and benzyl led to the isolation of a thianthreniumyl perchlorate (i.e., **1c**,**d**,**f**). Oxidations at the 4:1 molar ratio produced $Hg(ClO_4)_2$, which formed a partly insoluble complex (**2**) with thianthrene having the composition $Th_3Hg(ClO_4)_2$. This product could be isolated if removed before workup treatment with aqueous 4 M LiCl, which, otherwise caused its decomposition into its components. The complex **2** was also prepared directly from reaction of Th with $Hg(ClO_4)_2$ in acetonitrile. Oxidation of benzylmercuric chloride by $Th^{\bullet+}ClO_4^-$ in methylene chloride solution also occurred quantitatively, giving benzyl chloride, 1- and 2-benzylthianthrene, and a mixture of dibenzylthianthrenes. Oxidation of *t*-BuHgCl in acetonitrile solution led to a quantitative mixture of isobutene, *t*-BuOH, and *t*-BuNHAc. $Th^{\bullet+}ClO_4^-$ also oxidized metallic Hg to either Hg^+ or Hg^{2+}, depending on the amount of oxidant used.

Some years ago it was found that the thianthrene ($Th^{\bullet+}$) and phenoxathiin cation radicals reacted with some diarylmercurials and with dimethyl- and diethylmercury according to eq 1.[2] In this equation, R represented then



either a phenyl ring bearing an electron-donor group or methyl and ethyl. The mechanism of this reaction has never been satisfactorily defined. The possibility that reaction begins with electron transfer and formation of a very labile diorganomercurial cation radical was discussed by Sugiyama and Shine.[3] These workers found circumstantial evidence for radical formation in the reaction of diethylmercury (Et_2Hg) with $Th^{\bullet+}ClO_4^-$ under $^{18}O_2$. That is, labeled thianthrene 5-oxide (ThO) and 5,10-dioxide (ThO_2) were obtained and their formation was attributed to transfer of oxygen from the labeled ethylperoxy radical ($EtO_2^\bullet$), formed by trapping of $Et^\bullet$ with oxygen, to the Th or $Th^{\bullet+}$ nucleus. At the same time small amounts of ^{18}O-labeled ethanol and acetaldehyde were obtained and were attributed also to decomposition of labeled $EtO_2^\bullet$. The steps thus formulated were modeled on the earlier work of Kochi and co-workers in the reactions of dialkylmercurials with hexachloroiridium(IV) ion.[4] In that work rate-limiting formation of $R_2Hg^{\bullet+}$ occurred, whose rapid decomposition led to alkyl radicals ($R^\bullet$). A distinction was made between the reactions occurring by electron transfer and by electrophilic cleavage of an alkyl–mercury bond.[4] The formation of 5-substituted thianthreniumyl perchlorates (1) was interpreted subsequently, then, at least insofar as R = Et was concerned, as occurring as in eqs 2–4.[2] Preference was given to the electron-transfer route as compared with one involving direct electrophilic displacement, shown in abbreviated form in eqs 5 and 6. In the last equations a sulfuranyl radical is formed but is rapidly oxidized by a second cation radical. The stoichiometry of the two routes is, of course, the same.



$$R_2Hg^{\bullet+} \longrightarrow R^\bullet + RHg^+ \quad (3)$$

$$4Th^{\bullet+} + R_2Hg \longrightarrow 4Th + 2R^+ + Hg^{2+} \quad (7)$$

We have now sought, and obtained, supporting evidence for the electron-transfer pathway by working with the series of unsymmetrical ethyl-, isopropyl-, and *tert*-butylmercurials, MeHgEt, MeHg-*i*-Pr, and MeHg-*t*-Bu. The basis of this approach is to be found again in the works of Kochi and co-workers on the absence of steric constraints in outer-sphere electron transfer[5,6] and hinges on steric arguments. If reaction of these diorganomercurials followed the displacement route, the sterically easier displacement of Me should lead in each case to 5-methylthianthreniumyl perchlorate (**1a**) and RHg^+. On the other hand, the electron-transfer route should lead in each case to the better stabilized $R^\bullet$ and $MeHg^+$. The $R^\bullet$ would then be either trapped or oxidized by $Th^{\bullet+}$ The crux of the comparison of routes would be finding the Me group of MeHgR either solely as **1a** or solely as $MeHg^+$.

The stoichiometry shown in eq 1 is of the kind usually found in reactions of nucleophiles with $Th^{\bullet+}$, its analogues, and polynuclear aromatic cation radicals,[7,8] that is, a 2:1 ratio of cation radical to nucleophile, needed, of course, for eventual pairing of electrons in products. In the course of this work we have found that some dialkylmercurials, e.g, di-*tert*-butyl-, dibenzyl-, and diallylmercury, are oxidized more extensively by $Th^{\bullet+}$ with a 4:1 stoichiometry, summarized in eq 7.

Results

In the writing that follows, references will be made to 5-R-thianthreniumyl perchlorates (**1a–g**) in which R is Me (**1a**), Et (**1b**), *i*-Pr (**1c**), *t*-Bu (**1d**), Bu (**1e**), benzyl (**1f**), and allyl (**1g**). However, it will be seen that only **1a**,**b**,**e**,**g** were isolated.

Reactions of $Th^{\bullet+}ClO_4^-$ with MeHgR. Reactions were carried out by adding MeHgR either neat or in acetonitrile to a solution/suspension of $Th^{\bullet+}ClO_4^-$ in the same solvent under argon. Additions were made with a microsyringe, in effect titrating the $Th^{\bullet+}$ with the diorganomercurial. Each reaction (R = *t*-Bu, *i*-Pr, Et) was complete at the 2:1 ratio of $Th^{\bullet+}$/MeHgR. Following completion of reaction, a small aliquot of aqueous 4 M LiCl was injected, the purpose of which was to convert $MgHg^+$ (or RHg^+, whichever had been formed) into covalent MeHgCl (or RHgCl). The addition of aqueous LiCl also resulted in the conversion of other cations or potential cations (R^+) into the corresponding RCl and ROH. Further, $RNHCOCH_3$ was also formed by quenching of solvent-derived $RN{=}C^+CH_3$ with the water solution. Thus, a variety of products was formed both from direct reaction and the workup procedure. They were assayed by gas chromatography (GC) on a number of columns and are listed in Table I.

Prominent of our findings is the formation of MeHgCl in large yield in each reaction (runs 1, 2, and 4). We could not find any other alkylmercuric chloride (RHgCl) by GC. Small amounts of alkane (RH) and relatively larger amounts of alkene (R(–H)) were obtained for R = *t*-Bu and *i*-Pr. The bulk of the alkene is thus attributable to deprotonation of R^+ rather than to disproportionation of $R^\bullet$ by which reaction equal amounts of alkane and alkene would have been formed. The relative amounts of ROH, RCl, and $RNHCOCH_3$ vary from one case to another. Insofar as RCl is concerned, we feel confident that in the case of MeHgEt, EtCl was formed by displacement of the ethyl group from the 5-ethylthianthreniumyl ion (the perchlorate, **1b**). The formation of **1b** and its reaction with

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Table I. Products of Reaction of MeHgR with $Th^{\bullet+}ClO_4^-$ in Acetonitrile

		reactants, mmol		products, mmol and %[a]												
run	R	MeHgR	$Th^{\bullet+}$-ClO_4^-	RH	R(–H)	ROH	RCl	RNHC-OCH_3	MeHgCl	Th	ThO	1-RTh[b]	2-RTh[b]	R_2Th[c]	remarks
1	*t*-Bu	0.290	0.583		0.111	0.087	0.018	0.068	0.277	0.519	0.050				*d*
					38.3	30.0	6.2	23.4	95.5	89.0	8.6				
2	*i*-Pr	0.514	1.028	0.004	0.092		0.177	0.145	0.485	0.935		0.013	0.065	0.012	
				0.80	17.9		34.4	28.2	94.4	91.0		1.3[e]	1.3[e]	1.2[e]	
3	*i*-Pr	0.121	0.483	0.001	0.017	0.005	0.006	0.070	*f*	0.349	0.114	0.003	0.013	0.003	*g*
				0.83	14.0	4.1	5.0	57.9		72.3	23.6	0.62[e]	2.7[e]	0.62[e]	
4	Et	0.498	0.996	0.001	0.002		0.249	0.095	0.454	0.873		0.026	0.072	0.012	
				0.20	0.40		50.0	19.1	91.2	87.7		2.6[e]	7.2[e]	1.2[e]	

[a] Percent yields are given in the second entry of each run. [b] The position of R in RTh is assumed, based on relative yields. [c] Assumed from GC–MS to be R_2Th. GC yields are the sum of several peaks of isomeric R_2Th. [d] Di-*tert*-butyl peroxide (0.001 mmol (0.3%)) was also obtained. [e] Percent yield based on amount of $Th^{\bullet+}$. [f] Not measured. [g] 2,3-Dimethylbutane (0.0004 mmol (0.33%)) was also obtained.

4 M LiCl were shown to occur in separate experiments, dealt with later. However, we were unable to find, in separate experiments, the 5-isopropyl- (**1c**) and 5-*tert*-butylthianthreniumyl (**1d**) perchlorates and attribute, therefore, the products ROH and RCl in Table I to reactions of $RClO_4$ (R = *i*-Pr and *t*-Bu) with the added aqueous LiCl solution.

Most of the $Th^{\bullet+}$ used in these reactions was recovered as thianthrene (Th). This must have been formed in two ways: one from reduction of $Th^{\bullet+}$ by MeHgR and the other either by reduction of $Th^{\bullet+}$ by $R^\bullet$ or, during workup, by displacement of R^+ from 1 by Cl^-, e.g., as in the case of **1b**.

Table I also lists alkyl- and dialkyl-substituted thianthrenes, 1-RTh, 2-RTh, and R_2Th. These were formed in the reactions of $Th^{\bullet+}ClO_4^-$ with MeHg-*i*-Pr and MeHgEt and were identified as to molecular weight by GC–MS. The assignments 1-RTh and 2-RTh in Table I were made only on the basis of what we should expect if the products had been formed by addition of $R^\bullet$ to the ring positions of $Th^{\bullet+}$ (Scheme I). That is, the 2-position in $Th^{\bullet+}$ has the higher spin density[9] and is the position at which reaction with $R^\bullet$ is, therefore, more likely to occur. We know, however, and will present the evidence later that 1- and 2-EtTh may not only have been formed directly, as shown, but were present also in the mixture of products in the form of 1,5- and 2,5-diethylthianthrenium perchlorates, from which 1-EtTh and 2-EtTh were obtained by displacement of the 5-ethyl group in the workup reaction with Cl^-. The mode of formation of 1,5- and 2,5-diethylthianthrenium ions is illustrated in Scheme I (R = Et). As for R_2Th (R = Et, *i*-Pr), several isomers were found by GC and identified as to molecular weight by GC–MS. The structures are unknown.

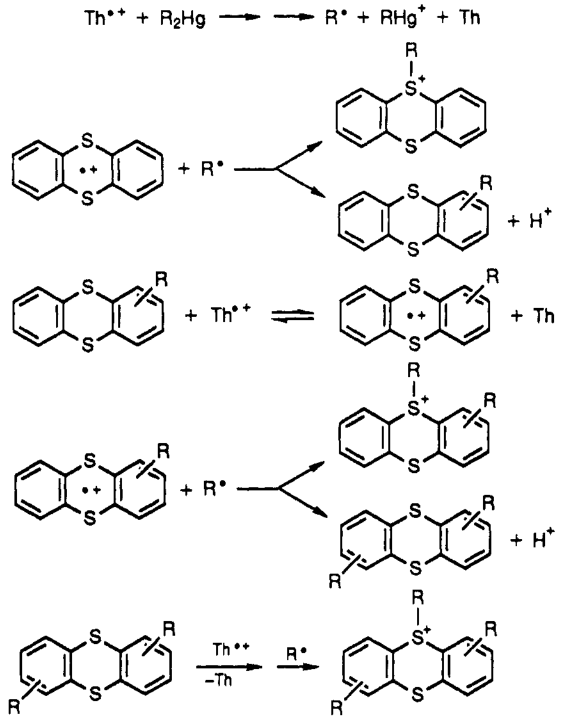
All of the products listed in Table I were assayed by quantitative GC with the help of authentic samples and internal standards, except for 1-RTh, 2-RTh, and R_2Th, for which the response factor of Th was used.

Table I also lists thianthrene 5-oxide (ThO). It was formed in small amount in the reaction with MeHg-*t*-Bu and larger amount in one reaction with MeHg-*i*-Pr (run 3). ThO was formed by the well-known reaction of $Th^{\bullet+}$ with water (eq 8),[7,8] which was either present adventiously

$$2Th^{\bullet+} + H_2O \rightarrow Th + ThO + 2H^+ \qquad (8)$$

or added during workup. Formation of ThO was expected in run 3, in which an excess of $Th^{\bullet+}ClO_4^-$ was used deliberately to find if oxidation beyond the 2:1 ratio would occur. In the event, oxidation of MeHg-*i*-Pr stopped at the 2:1 ratio. The amount of ThO obtained (0.114 mmol)

Scheme I



after workup is equatable (eq 8) to there having been an excess of 0.228 mmol of $Th^{\bullet+}$, which corresponds well with the excess (0.242 mmol) that was used. Run 3 demonstrates, in fact, that reaction with MeHg-*i*-Pr leads exclusively to *i*-Pr^+ and $MeHg^+$, in which the latter has no propensity for further oxidation.

The material balances in Table I are summarized in Table IV (runs 1–4), where it can be seen that an excellent account of all units in the reactants was obtained. The account includes small amounts of side products such as di-*tert*-butyl peroxide from reaction of MeHg-*t*-Bu and 2,3-dimethylbutane from reaction of MeHg-*i*-Pr. These products are also diagnostic of radicals *t*-$Bu^\bullet$ and *i*-$Pr^\bullet$ having been formed.

Reactions with R_2Hg in the 4:1 Ratio. Table II lists the products of reaction of $Th^{\bullet+}ClO_4^-$ with di-*tert*-butyl-, dibenzyl-, and diallylmercury. With each of these mercurials reaction could be carried beyond the co-called normal 2:1 stoichiometry to one in which 4 mol of $Th^{\bullet+}$ could be used for 1 mol of R_2Hg. This stoichiometry calls for the complete oxidation of R_2Hg into R^+ and Hg^{2+}, and for the most part, the products in Table II bear this out. Much of the mercury in R_2Hg ended as Hg^{2+}, although some (runs 6, 10, and 11) remained at the Hg^+ level and was isolated (by workup with LiCl) as Hg_2Cl_2. One striking

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Table II. Products of Reactions of R_2Hg with $Th^{\bullet+}ClO_4^-$ and $Th^{\bullet+}BF_4^-$ in Acetonitrile

			reactants, mmol		products, mmol and %[a]												
run[b]	R	X^-	R_2Hg	$Th^{\bullet+}X^-$	RH	R(–H)	ROH	RCl	$RNHCOCH_3$	Th	ThO	Hg_2Cl_2	HgO	Hg	1	2	remarks
5	*t*-Bu	ClO_4^-	0.509	1.01	0.005	0.068	0.526	0.007	0.337[c]	0.998	0.015	0.231[c]					*d*
					0.49	6.7	51.7	0.69	33.1	97.8	1.5	90.8					
6	*t*-Bu	ClO_4^-	0.254	1.02	0.015	0.030	0.194	0.041	0.220[c]	0.560	0.010	0.014[c]	0.085			0.135[c]	
					3.0	5.9	38.2	8.1	43.3	55.2	1.0	11.0	33.5			39.9[e]	
7	*t*-Bu	BF_4^-	0.505	1.01	0.005	0.057	0.302		0.517	0.880	0.111	0.023[c,f]		0.467[c,f]			*d*
					0.50	5.6	29.9		51.2	87.2	11.0	9.1		92.4			
8	*t*-Bu	BF_4^-	0.351	0.70	0.011	0.091	0.313	0.058	0.205	0.598	0.067	0.013[c,f]		0.310[c,f]			*d*
					1.6	13.0	44.5	8.3	29.2	85.4	9.6	7.4		88.3			
9	Benz[g]	ClO_4^-	1.03	4.00			0.012	1.19	0.394	3.76	0.025		0.983[c]				*h*
							0.58	57.8	19.1	94.0	0.63		95.4				
10	Benz[g]	ClO_4^-	0.157	0.628			0.017	0.008	0.223	0.189	0.001	0.010[c]				0.134[c]	*i*
							5.4	2.5	71.0	30.1	0.16	12.7				64.0[j]	
11	allyl	ClO_4^-	0.79	3.2						0.658		0.183[c]			1.24[c]	0.408[c]	
										20.6		46.3			38.8	38.1[k]	

[a] Percent yields are given in the second entry of each run. Yields of compounds containing group R are based on two R groups per R_2Hg. Yields of compounds of Hg are based on the Hg content of R_2Hg, except for **2**. Yields were measured by GC except where stated (footnote *c*). [b] Runs are numbered sequentially beginning with Table I. [c] Isolated yield. [d] Di-*tert*-butyl peroxide was also obtained as follows. Run 5, 0.012 mmol (1.2%); run 7, 0.020 mmol (2.0%); run 8, 0.002 mmol (0.02%). [e] Based on $Th^{\bullet+}$; yield based on Hg is 53.1%. [f] Metallic Hg was obtained mixed with Hg_2Cl_2. The Hg was removed by dissolving in HNO_3, leaving Hg_2Cl_2. The HNO_3 solution was made alkaline with NaOH. The HgO thus obtained was isolated and is the basis for expressing the yield of metallic Hg. [g] Benzyl. [h] Also obtained were $(PhCH_2)_2$ (0.09 mmol (8.7%)), 1-$PhCH_2Th$ (0.04 mmol (1.0%)), 2-$PhCH_2Th$ (0.212 mmol (5.3%)), and $(PhCH_2)_2Th$ (sum of four GC peaks, 0.026 mmol (1.3%)). Yields are based on $Th^{\bullet+}$. [i] Also obtained were $(PhCH_2)_2$ (0.008 mmol (5.1%)), 1-$PhCH_2Th$ (0.005 mmol (0.8%)), and 2-$PhCH_2Th$ (0.029 mmol (4.6%)). Yields are based on $Th^{\bullet+}$. [j] Based on $Th^{\bullet+}$; yield based on Hg is 85.4%. [k] Based on $Th^{\bullet+}$; yield based on Hg is 51.6%.

result of the 4:1 oxidation was the formation of a complex (**2**) between Th and Hg^{2+} (eq 9). The complex had limited

$$3Th + Hg(ClO_4)_2 \rightarrow \underset{\mathbf{2}}{Th_3Hg(ClO_4)_2} \qquad (9)$$

solubility in CH_3CN and precipitated from the reaction solution. The complex was decomposed immediately by addition of water and could be isolated, therefore, only if it was removed from the reaction mixture before any of the workup steps were taken. This distinction can be seen in runs 9 and 10. In the former, workup by injection of aqueous 4 M LiCl destroyed the complex, converting it into Th and (presumably) hydrated Hg^{2+}. The Hg^{2+} was thus freed from **2** for later isolation (by workup with NaOH) as HgO. In run 10, however, **2** (representing 85% of the Hg^{2+} and 64% of the Th) was removed before workup with 4 M LiCl. In this case, too, the remainder of the mercury in the $(PhCH_2)_2Hg$ was obtained as Hg^+, oxidation having, apparently, not gone to completion. Product **2** (representing 53% of the mercurial) was obtained from the reaction of *t*-Bu_2Hg (run 6), yet nearly 34% of the Hg^{2+} that had been formed was isolated as HgO. The reason for this is undoubtedly the partial solubility of **2** and its incomplete removal from the reaction solution. The **2** that remained in solution was decomposed by subsequent workup injections, freeing Hg^{2+} for recovery as HgO. Our data for the reaction of diallylmercury are not as complete as in the other cases. A large amount (46%) of the mercury content remained at the Hg^+ level, but we do not know why. The diallylmercury reaction differs from the others, too, in the formation and isolation (39%) of 5-allylthianthreniumyl perchlorate (**1g**). Persistent attempts to find and isolate the corresponding 5-*tert*-butyl (**1d**) and 5-benzyl (**1f**) analogues failed.

Table II lists four runs with *t*-Bu_2Hg, one of which (run 6) has been dealt with. Run 5 was carried out at the 2:1 level. Formation of **2** did not occur. Nevertheless, oxidation went beyond the 2:1 stoichiometry, and 90% of the mercury in the *t*-Bu_2Hg was taken to the Hg^+ level. We have not traced the oxidant responsible, but it arose from our using ClO_4^- as the counterion, as can be deduced from the reactions with $Th^{\bullet+}BF_4^-$, runs 7 and 8. Each of these was carried out in the 2:1 stoichiometry. Reaction occurred rapidly with the formation of the usual type products (isobutene, *t*-BuOH, *t*-BuCl, *t*-$BuNHCOCH_3$), accounting for 90 and 95% of the *t*-Bu groups in the *t*-Bu_2Hg. Metallic mercury also formed to the extents of 88 and 92% and was recovered eventually as HgO. Small amounts (9 and 11%) of the mercury in the *t*-Bu_2Hg ended also as Hg^+. It is clear that *t*-$BuHg^+$ (i.e., *t*-$BuHg^+BF_4^-$) formed in the first electron transfer (eqs 2 and 3) does not survive but must decompose into *t*-Bu^+ and Hg. In contrast to the use of $Th^{\bullet+}ClO_4$, further oxidation was not extensive. The stoichiometry of reaction of *t*-Bu_2Hg with $Th^{\bullet+}BF_4^-$ is summarized in eq 10.

$$2Th^{\bullet+}BF_4^- + t\text{-}Bu_2Hg \rightarrow 2Th + 2t\text{-}Bu^+BF_4^- + Hg^0 \qquad (10)$$

Small amounts of other products were obtained from these diorganomercurials, attesting probably to the formation of radicals, $R^\bullet$. Thus, di-*tert*-butyl peroxide was obtained in runs 5, 7, and 8, and bibenzyl (8.2 and 5.1%, respectively) in runs 9 and 10. Reactions with $(PhCH_2)_2Hg$ also gave substitution products 1- and 2-$PhCH_2Th$ and $(PhCH_2)_2Th$, identified as to molecular weight by GC–MS and assayed by GC and the use of the response factor for Th.

Reactions of Me_2Hg, Et_2Hg, and Bu_2Hg with $Th^{\bullet+}$-ClO_4^-. These reactions were carried out primarily as controls for comparison with reactions of MeHgR and those of R_2Hg that went to the 4:1 oxidation level. Also, insofar as Et_2Hg is concerned, our earlier work resulted in a 30% yield of **1b** and an excessive yield of Th.[2] The interpretation of those results was that a large part of reaction took place at the 1:1 level of reactants (eqs 2 and 3) and that ethyl radicals thus formed escaped further reaction with $Th^{\bullet+}$.[2] It now seemed that that interpretation could be wrong and needed to be checked.

Reactions with these dialkylmercurials (R = Me, Et, Bu) occurred at the 2:1 level. This is particularly noticeable in the reactions of Bu_2Hg (runs 14 and 15, Table III) in which a 0.50-mmol excess of $Th^{\bullet+}ClO_4^-$ was used. The excess of $Th^{\bullet+}$ remained after reaction with Bu_2Hg was complete, to be hydrolyzed in workup into ThO. From 0.50 mmol of $Th^{\bullet+}$ 0.25 mmol of ThO (and of Th) is expected and corresponds with what was found in each run, namely,

Table III. Products of Reaction of R_2Hg with $Th^{\bullet+}ClO_4^-$ in Acetonitrile

		reactants, mmol		products, mmol and %[a]										
run[b]	R	R_2Hg	$Th^{\bullet+}ClO_4^-$	RH	R(–H)	R–R	RCl	RHgCl	1	Th	ThO	1-RTh[d]	2-RTh[d]	R_2Th[e]
12	Me	1.00	2.01					0.849	0.767[c]	0.982	0.013	tr	tr	tr
								42.5	38.1	48.9	0.65			
13	Et	0.260	0.511		0.005	0.002	0.151	0.258	*f*	0.406		0.012	0.041	0.008
					0.96	0.77	29.0	49.6		79.5		2.3	8.0	1.6
14	Bu	1.00	2.50	0.018	0.001	0.008	0.811	0.982	*f*	2.107	0.244	0.020	0.106	0.029
				0.90	0.05	0.40	40.6	49.1		84.3	9.8	0.80	4.2	1.2
15	Bu	1.00	2.50				0.695[g]	0.901	*f*	2.103	0.245	0.024	0.111	0.027
							34.8	45.1		84.1	9.8	0.96	4.4	1.1

[a] Percent yields are given in second entry of each run. The yields of products containing group R are based on the amount of R group in R_2Hg, except for 1-RTh, 2-RTh, and R_2Th whose yields are based on $Th^{\bullet+}ClO_4^-$. [b] Runs are numbered sequentially from Table I. [c] **1a**, isolated. [d] Position of R in RTh is assumed, based on relative yields. [e] Assumed from GC–MS. GC yields are sum of several peaks from isomeric R_2Th. [f] Not isolated. This product was converted into RCl and Th by reaction with LiCl in workup. [g] Obtained by treating isolated mixture of sulfonium perchlorates with LiCl.

Table IV. Summary of Material Balances (%) and Stoichiometry for Reactions of Organomercurials with Thianthrene Cation Radical in Acetonitrile[a]

run	stoichiometry[b]	Th from $Th^{\bullet+}X^-$	R groups from R_2Hg	Me group from MeHgR	R group from MeHgR	units of Hg
1	2:1	97.6		95.5	97.9	
2	2:1	99.7		94.4	101.1	
3	2:1	99.8		*c*	99.9	
4	2:1	98.7		91.2	94.2	
5	2:1	99.3	92.7			90.8[d]
6	4.1	96.1	98.5			97.6[e]
7	2:1[f]	98.2	87.2			101.5[g]
8	2:1[f]	95.0	96.6			95.7[g]
9	4:1	94.6	86.2			98.3[h]
10	4:1	99.5	89.7			98.1[j]
11	4:1	97.5	*i*			102.4[j]
12	2:1	87.7	80.6			84.9[k]
13	2:1	91.4	93.6			99.2[k]
14	2:1	100.3	99.3			98.2[k]
15	2:1	100.4	89.3			90.2[k]

[a] Summations of Th units in all products containing Th and based on initial amount of $Th^{\bullet+}X^-$; of R units in products containing R group and based on the number of R units in R_2Hg and MeHgR; of Hg units in all mercury-containing products; of the Me group obtained as MeHgCl from MeHgR. [b] The ratio $Th^{\bullet+}$:organomercurial operative in the reaction. [c] Not measured. [d] As Hg_2Cl_2. [e] As a combination of Hg_2Cl_2, HgO, and compound **2**. [f] $X^- = BF_4^-$. In all other cases, $X^- = ClO_4^-$. [g] As a combination of Hg_2Cl_2 and metallic Hg. [h] As HgO. [i] Only the allyl group in **1** was measured, 25.8% of (allyl)$_2$Hg. [j] As a combination of Hg_2Cl_2 and compound **2**. [k] As RHgCl only.

0.244 and 0.245 mmol, respectively. Formation of 5-R-thianthreniumyl perchlorate is to be expected in each of these reactions (R = Me, Et, Bu), too. This was what was obtained from reaction of Me_2Hg (run 12), in which the workup procedure was that of our earlier practice, that is, the use of 1% (ca. 0.25 M) aqueous LiCl designed to convert $MeHg^+$ into MeHgCl. In the workup procedure for reactions of Et_2Hg (run 13) and Bu_2Hg (run 14), however, 4 M LiCl was used and the concentration of Cl^- was sufficient to convert the sulfonium products (**1b**,**e**) into Th and alkyl chloride. The formation of **1b** in reaction of Et_2Hg (and MeHgEt) was confirmed in separate experiments by its isolation. Its reaction with Cl^- was also confirmed. That is, when the earlier procedure[2] was used (see Experimental Section), crude **1b** was isolated in 58% yield from reaction of Et_2Hg and in 59% yield from reaction of MeHgEt. The crude **1b** was converted subsequently into Th (89%) and EtCl (91%) by reaction with 4 M LiCl. It was found, furthermore, that reaction of crude **1b** with Cl^- gave 1- and 2-ethylthianthrene in collective yield (GC) of 9%, indicative of the presence of 1,5- and 2,5-diethylthianthreniumyl perchlorates in the isolated, crude **1b**. The presence of signals from these salts was also found in the ^1H NMR spectrum of crude **1b** obtained from MeHgEt. Purification of **1b** was achieved by successive reprecipitation from CH_2Cl_2 solution with ether.

The formation of mixed sulfonium salts was also found in reaction of Bu_2Hg (run 15). In that case, the mixture of sulfonium salts was isolated by preparative-scale TLC and converted into BuCl by reaction with solid LiCl in CH_3CN. The amount of BuCl formed (0.695 mmol) corresponded very well with the sum (0.657 mmol) of Th and butylthianthrenes obtained.

It is noticeable (Table III) that in these reactions only small amounts of hydrocarbon products, RH, R(–H), and RR, were obtained, indicative of the small extent of free radical ($R^\bullet$) reactions. Also absent from Table III are *N*-alkylacetamides. The same is true of reactions of MeHgEt and Et_2Hg designed for isolation of **1b**. This is discussed later.

Reaction of $PhCH_2HgCl$ with $Th^{\bullet+}ClO_4^-$ in CH_2Cl_2. Titration addition of a solution of $PhCH_2HgCl$ in CH_2Cl_2 to a solution of $Th^{\bullet+}ClO_4^-$ in that solvent caused the rapid discharge of the $Th^{\bullet+}$ color. Reaction was complete at the 2:1 molar ratio. Quenching with solid KCl led to a considerable amount (69% conversion) of $PhCH_2Cl$ (Table V). The balance of $PhCH_2$ units (28.3% conversion) ended up attached to thianthrene rings, as compared with 15% from reaction of $(PhCH_2)_2Hg$ (run 9). Neither benzyl alcohol nor bibenzyl was found, and, of course, since the solvent was CH_2Cl_2, benzylacetamide could not be a product. Thus, oxidation occurred readily and led to Hg^{2+} (isolated as HgO, 92.8%) and products attributable to benzyl groups at the $PhCH_2^+$ oxidation state.

Reaction of *t*-BuHgCl with $Th^{\bullet+}ClO_4^-$ in CH_3CN. Oxidation of *t*-BuHgCl occurred quickly at the 2:1 $Th^{\bullet+}ClO_4^-$/*t*-BuHgCl ratio. Almost all (97.5%) of the *t*-Bu groups were accounted for as a mixture of isobutene

Table V. Products of Reaction of t-BuHgCl[a] and $PhCH_2HgCl$[b] with $Th^{\bullet+}ClO_4^-$

	% yield from RHgCl	
product type	R = $PhCH_2$	R = t-Bu
R(-H)		10.8
RCl	65.4	
ROH		17.1
RNHAc		69.5
Th	86.5	95.6
ThO	0.5	3.6
1-RTh	3.7[c]	
2-RTh	16.6[c]	
R_2Th	6.4[c]	
RHgCl	5.6[d]	
Hg_2Cl_2		58.4
HgO	92.8	40.0

[a] In CH_3CN. [b] In CH_2Cl_2. [c] Percent based on initial $PhCH_2HgCl$; percents based on $Th^{\bullet+}ClO_4^-$ were, in sequence, 1.85, 8.3, and 1.6. [d] Recovered.

(10.8%), t-BuOH (17.1%), and t-BuNHAc (69.5%). Instead of finding all of the mercury as the H^{2+} state, however, only 40% was obtained as HgO while the remainder (58.4%) was isolated as Hg_2Cl_2.

Reactions of $Th^{\bullet+}ClO_4^-$ with Metallic Mercury. Hg was oxidized quickly when broken into fine droplets by sonification under a solution of $Th^{\bullet+}ClO_4^-$ in acetonitrile. Oxidation was primarily to the Hg^+ level when Hg was in excess and to the Hg^{2+} level when the $Th^{\bullet+}/Hg$ molar ratio was 2:1. The yellow complex **2** was formed, particularly under the latter condition.

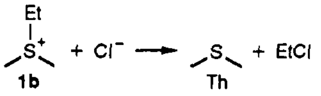
Discussion

Reactions of MeHgR. In the three cases of unsymmetrical mercurials (R = Et, i-Pr, t-Bu) the R group underwent cleavage from mercury. MeHgCl was obtained in yields of ca. 91–96%, signifying the formation of $MeHg^+$ that was converted by later workup with LiCl into MeHgCl. There is little doubt, therefore, that these results are diagnostic of an electron-transfer reaction (eqs 2 and 3) rather than a displacement reaction (eq 5). The distinction between cleavage of a t-Bu group (in MeHg-t-Bu) and a methyl group (in Me_2Hg) by $IrCl_6^{2-}$ has been documented by Kochi and co-workers,[4] who showed that the preferred cleavage of t-Bu was diagnostic of an electron-transfer reaction and inconsistent with direct attack on the alkyl–mercury bond. In the series MeHgR (R = Et, i-Pr, t-Bu) Kochi and co-workers found that exclusive cleavage of the i-Pr and t-Bu groups and preferential cleavage of the Et group from the mercurial occurred. In our own work no evidence for cleavage of the Me–Hg bond could be found, based on the failure to find by GC analysis either RHgCl or products of methyl radical reactions. The fate of $R^\bullet$ radicals formed by cleavage of the R–Hg bond can be deduced from the workup procedure and the nature of the products listed in Table I, as well as from further experiments with MeHgEt and Et_2Hg (Experimental Section). Workup involved the addition of 4 M aqueous LiCl to the reaction mixture after reaction was complete. Consequently, the products obtained from MeHg-t-Bu and MeHg-i-Pr are those of R^+, namely, the alkene, ROH, $RNHCOCH_3$, and RCl. It is apparent that most of the radicals $R^\bullet$ in these cases are oxidized (eq 11) rather than


(11)

trapped (eq 4) by $Th^{\bullet+}$. Analogous oxidations were reported in the reactions of MeHgR with $IrCl_6^{2-}$.[4] We were unable to find any evidence of trapping of t-$Bu^\bullet$ and i-$Pr^\bullet$ radicals at the sulfur atom of $Th^{\bullet+}$. Thus, the sulfonium salts **1c** and **1d** (R = i-Pr and t-Bu) are unknown to us. At the same time, small amounts of 1- and 2-isopropylthianthrene (i-PrTh) and of diisopropylthianthrenes (i-Pr_2Th) were found, and these may well have resulted from trapping of i-$Pr^\bullet$ radical at the ring positions of $Th^{\bullet+}$ (Scheme I). We have speculated here that the i-PrTh formed in the greater amount (Table I) is the 2-isomer on the basis that the spin density at the 2-position is greater than at the 1-position of $Th^{\bullet+}$.[9] Three isomers of i-Pr_2Th were detected by GC and GC–MS, and the sum of their yields is given in Table I. The formation of i-Pr_2Th and i-PrTh is discussed later.

Table I shows that of the Et groups in MeHgEt, 50% ended as EtCl and 19% as $EtNHCOCH_3$. It is unlikely that the latter product could be formed in any other way than by reaction of Et^+ with solvent CH_3CN. Therefore, $Et^\bullet$ radicals were oxidized by $Th^{\bullet+}$ (eq 11). It is unlikely, however, that the EtCl was formed by the delayed reaction of Et^+ (or $EtClO_4$) with LiCl added in the workup. Instead, we believe that the sulfonium salt **1b** (R = Et) was, in fact, formed by trapping of Et radical by $Th^{\bullet+}$, only to be converted later into EtCl and Th by added LiCl (eq 12).


(12)

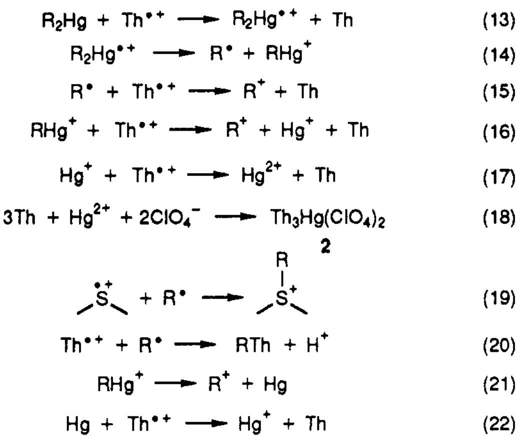
The sulfonium salt (**1b**), was, in fact, prepared and isolated in 59% yield (before purification) from a separate reaction of MeHgEt and in 58% yield from a separate reaction of Et_2Hg with $Th^{\bullet+}ClO_4^-$. Reaction of the unpurified **1b** with 4 M LiCl gave EtCl and Th in 93.3 and 93.5% yields, respectively. Interestingly, the reaction with LiCl gave also the two isomers of EtTh, the significance of which is discussed later.

The overall results of reactions of MeHgR with $Th^{\bullet+}ClO_4^-$ are consistent, therefore, with an initial electron-transfer step. Formation of $R^\bullet$ radicals ensued, and they either were trapped by $Th^{\bullet+}$ at sulfur ($Et^\bullet$) and ring positions ($Et^\bullet$, i-$Pr^\bullet$) or were oxidized to R^+ ($Et^\bullet$, i-$Pr^\bullet$, and t-$Bu^\bullet$). The cations R^+ were converted variously into alkene, ROH, $RNHCOCH_3$, and RCl with no discernible pattern, except in the understandable higher yields of isobutene and propene than ethene.

Reactions of R_2Hg. The reactions of dialkyl- and diarylmercurials with $Th^{\bullet+}ClO_4^-$ that were first discovered had the stoichiometry shown in eq 1, namely, a ratio of $2Th^{\bullet+}/R_2Hg$.[2] We have now found that oxidation can go to completion, namely, to a ratio of $4Th^{\bullet+}/R_2Hg$, depending on the nature of R. Thus, the earlier discoveries[2] of a 2:1 ratio were fortuitous in that the R_2Hg used had R groups unsuitable to 4:1 oxidation. Therefore, our present results are divided into two groups: those R_2Hg that can undergo the 4:1 oxidation (R = t-Bu, benzyl, and allyl (Table II)) and those whose oxidation remains at the 2:1 level (R = Me, Et, and Bu (Table III)). The difference in R groups is apparent; R_2Hg containing alkyl groups that give the more stabilized cations can undergo total oxidation (eq 7).

The 4:1 level of oxidation is best seen in run 6 (R = t-Bu) and runs 9 and 10 (R = benzyl). Although each of these oxidations was at the 4:1 level, the nature of the products of reaction depended in part on the nature of R and in part on the workup procedure used. During each of these reactions a yellow solid (**2**) formed and could be removed by filtration (runs 6 and 10). Thereafter, workup with 4 M aqueous LiCl gave the other products listed in Table II. If, on the other hand, aqueous LiCl was added before removal of **2** (run 9), the **2** decomposed and all products

Scheme II



went into solution for assay by GC. We shall show later that **2** is formed from coordination of Th with Hg^{2+} and has the structure $(Th)_3Hg(ClO_4)_2$. The overall sequence of reactions that can arise from a 4:1 level of oxidation is given, then, in Scheme II. The scheme shows in eqs 13–15 the oxidative decomposition of R_2Hg to which we have already referred. The cation RHg^+ is oxidized further, either as shown (eqs 16 and 17) or after decomposition into R^+ and Hg (eqs 21, 22, and 17).

We see, then, from Table II, run 6, that after allowing for disproportionation of t-Bu$^\bullet$ radicals (6%), 92.5% of the t-Bu groups in t-Bu_2Hg have ended as products of t-Bu$^+$. Much of the Th that was formed (39.9%) became complexed in **2**. Complexation of all of the Th that is formed cannot occur in these reactions because more Th is formed than required for **2**, namely, 4 mol per mol of Hg^{2+}. We should expect then to find 25% of the Th as free Th. However, more than that is listed in run 6. The reason for this is that **2** is partly soluble in CH_3CN, and that part which remains in solution is decomposed during workup. The decomposition of **2** leaves Hg^{2+} in solution, as can be shown by later treatment of the aqueous workup layer with NaOH, when HgO is formed. In run 6, 33.5% of the Hg in t-Bu_2Hg was obtained as HgO. Similarly, in run 9 >95% of the HgO was obtained, as contrasted with the result in run 10, in which **2** was isolated before workup with aqueous LiCl was carried out and represented >85% of Hg^{2+}.

Table II reports three other runs with t-Bu_2Hg, in each of which a molar ratio of 2:1 of $Th^{\bullet +}/t$-Bu_2Hg was used. In run 5 the oxidant was $Th^{\bullet +}ClO_4^-$. Nearly 98% of the $Th^{\bullet +}$ was converted into Th and nearly 92% of the t-Bu groups ended at the t-Bu$^+$ oxidation level. Nevertheless, the Hg in the t-Bu_2Hg was converted primarily (91%) into Hg^+ and was isolated as Hg_2Cl_2. Stoichiometrically, oxidation should have proceeded only to the Hg^0 level (eqs 13–15 and 21), so that another oxidant, possibly $HClO_4$, appears to be present in the $Th^{\bullet +}ClO_4^-$ system and to be called upon in appropriate circumstances. In contrast, two runs (7 and 8) with $Th^{\bullet +}BF_4^-$ and t-Bu_2Hg, each at the 2:1 reactant ratio, did end primarily as expected, in giving 92 and 88% of Hg^0, respectively, as well as a good accounting of t-Bu$^+$ groups (85 and 93%, respectively). Thus, oxidation by the $Th^{\bullet +}BF_4^-$ involves $Th^{\bullet +}$ only. Last, in Table II are the data for reaction with diallylmercury. A complete assay of the allyl groups was not made. The significant result insofar as the allyl group is concerned, though, was the formation of 5-allylthianthrenium perchlorate (**1g**) in nearly 39% yield. Thus, the allyl radical was trapped at a sulfur atom by $Th^{\bullet +}$, in contrast with the behaviors of t-Bu_2Hg and dibenzylmercury. The complex **2** was formed, accounting for nearly 52% of the Hg as Hg^{2+}. Perplexingly, the remainder (46%) of the Hg was obtained as Hg_2Cl_2, that is, in the Hg^+ state, for reasons unclear to us.

In contrast with the results reported in Table II, those in Table III are fully in accord with the 2:1 stoichiometry reported earlier.[2] The products are consistent with the formation and reactions of the radicals $R^\bullet$ and of the cations RHg^+. The latter were found as RHgCl after workup in yields ranging from 85 to 99% of theory. Evidence for the radicals $R^\bullet$ was found to a limited extent in the dimers butane (run 13) and octane (run 14). 5-Alkylthianthrenium perchlorates were formed also in good yield, but only the 5-methyl salt (**1a**) was isolated, in 77% yield. The sulfonium salts **1b** (R = Et) and **1e** (R = Bu) were not isolated in the series shown in Table III but were converted into RCl for more convenient assay and amounted (runs 13–15) to 58, 81, and 69% of theory. Our interpretation of the formation of **1a**,**b**,**e** is of trapping of $R^\bullet$ by $Th^{\bullet +}$. Measurable amounts of ring-substituted thianthrenes 1- and 2-RTh and R_2Th were obtained also from Et_2Hg and Bu_2Hg, and the origin of these products is regarded, again, as the trapping of $R^\bullet$.

It is noteworthy that in runs 14 and 15 a 25% excess of $Th^{\bullet +}ClO_4^-$ was used. Nevertheless, the excess was not involved in further oxidation of $BuHg^+$, but remained for later workup hydrolysis (eq 8). This is to be seen in the yields of ThO, representing in each run 98% of the 0.25 mmol expected from an excess of 0.50 mmol of $Th^{\bullet +}$.

An accounting of the fate of Et groups in the reaction Et_2Hg can be obtained from Table III. As expected, 50% of the Et groups are obtained as EtHgCl (run 13). In contrast, only 29% of the Et groups are found as EtCl. If this represents how much **1b** was formed, from which EtCl was derived in later reactions with added Cl^-, the yield of **1b** is, in fact, the same (30%) as was reported earlier.[2] The difference, then, between the earlier and current results is in the finding, now, of most of the remaining Et groups, that is, as ethene, butane, and the substituted thianthrenes. The yield of Th (0.406 mmol), in fact, corresponds well with what should have been formed (0.409 mmol) in converting Et_2Hg into EtHgCl (0.258 mmol) and, eventually from **1b**, EtCl (0.151 mmol).

Formation of RTh and R_2Th. Listed in Tables I and III, and noted in the footnotes to Table II, are the products 1- and 2-RTh and R_2Th. As indicated earlier these abbreviations denote alkyl- and dialkylthianthrenes. We understand them to be formed by trapping of $R^\bullet$ radicals at the ring positions of $Th^{\bullet +}$ (Scheme I). According to this understanding, the several isomers of R_2Th, having unspecified structures, must be formed from an alkylthianthrene cation radical, $RTh^{\bullet +}$, whose formation (Scheme I) is viewed as not being difficult. These alkylthianthrenes were present, however, not only in their neutral form but also as thianthreniumyl salts, for example, 1,5-dialkylthianthrenium perchlorate. The basis for this conclusion was the results of run 15 with Bu_2Hg and of separate experiments with Et_2Hg (Experimental Section). 5-Butylthianthrenium perchlorate (**1e**) was isolated by TLC from the mixture of products of run 15. The **1e** was impure, however, because on treatment with LiCl it gave not only Th (and BuCl) but also 1- and 2-BuTh and three isomers of Bu_2Th (and BuCl). The yield of BuCl (0.695 mmol) corresponded well, not with that of Th (0.536 mmol) but with the sum of yields of Th and its alkyl derivatives (0.657 mmol), the last yields (0.121 mmol) being assayed with the assumption that these derivatives had the same GC response factor as Th. Thus, the impure **1e** was a mixture of **1e** (primarily) and other ring-substituted thianthreniumyl perchlorates.

Similar results were obtained in the reaction of isolated, crude **1b** with LiCl in that not only Th but also 1- and 2-EtTh were formed.

Therefore, 1- and 2-RTh and isomers of R_2Th must have been formed in these instances from a mixture of sulfonium ions, as shown in Scheme I.

Stability of RHg^+ and Formation of 2. Among the products listed in Table II is the complex $Th_3Hg(ClO_4)_2$ (**2**). The composition of **2** was deduced from elemental analyses and from the quantitative assay of its decomposition by water into Th and Hg^{2+}. Not only was **2** isolable from reactions of some R_2Hg with $Th^{\bullet+}ClO_4^-$, but it was prepared directly from Th and $Hg(ClO_4)_2$, the latter being obtained in solution by drying a solution of its commercially available trihydrate. Decomposition of **2** from this source with water gave 99% of the anticipated Th and 99% of the anticipated Hg^{2+} as HgO. Decomposition of some samples of **2** obtianed from R_2Hg reactions was not as satisfactory as decomposition of **2** that was prepared from $Hg(ClO_4)_2$. The **2** from R_2Hg reactions often gave evidence of having some Hg^+ content in that small amounts of Hg_2Cl_2 were obtained by treating the aqueous decomposition solution with 4 N HCl. Further, the HgO obtained by treating the aqueous solution with NaOH was often a dirty orange, instead of yellow orange, and became dark or grayish on standing, symptomatic of the presence of both Hg^+ and Hg^{2+} oxides. We do not know the reason for these behaviors. It is notable, also, that small amounts of Hg_2Cl_2 were obtained in reactions of R_2Hg that, stoichiometrically, should have given only Hg^{2+} and pure **2** (Table II). Therefore, our general view of reactions leading to **2** is not as clear-cut as we would want it. There is no doubt that **2** is formed but in some occasions it was contaminated by an Hg^+ complex of unknown composition. In spite of that the amount of Th obtained by decomposition with water always suited the formula for **2**.

We were unable to find complexes of Th with Hg^{2+} described in the literature. Complexes of phenoxathiin[10] and of 1,4-thioxane[11] with $HgCl_2$ have been described. They are four-coordinate with structure L_2HgCl_2, each ligand being bonded by its sulfur atom. Our complex **2** is not suited to such a four-coordinate structure, and its structure is yet to be determined.

Because Hg^{2+} is needed for its formation, **2** could be formed only in reactions of R_2Hg in which RHg^+ was not stable to further oxidation. Among the R_2Hg we have investigated, only those with R = *t*-Bu, benzyl, and allyl had this property. When an oxidizable RHg^+ is formed we do not know if separation into R^+ and Hg precedes further oxidation or not. We have found that metallic Hg can be oxidized by $Th^{\bullet+}$ to either the Hg^+ or Hg^{2+} level, depending on the relative amounts of reactants used. We found also that oxidation of $t\text{-}Bu_2Hg$ by $Th^{\bullet+}BF_4^-$ in the so-called 2:1 stoichiometry gave substantial amounts of Hg (Table II), signifying that $t\text{-}BuHg^+$ was unstable in those circumstances. Kochi and co-workers found that oxidation of $t\text{-}Bu_2Hg$ with $IrCl_6^{2-}$ could be carried to completion by more than a 4 molar ratio of $IrCl_6^{2-}$ but could also be stopped at the $t\text{-}Bu^+$ and $t\text{-}BuHg^+$ level if only 2 equiv of $IrCl_6^{2-}$ was used.[4] Reaction was carried out, as in our work, in CH_3CN, and the yield of $t\text{-}BuHg^+$ was measured by ^1H NMR spectroscopy after replacement of the solvent with pyridine. It is probable that in that work the $t\text{-}BuHg^+$ was stabilized by coordination with Cl^-, however. The NMR parameters reported for that assay were δ 1.43 and $J_{Hg-C-CH_3} = 256$ Hz. We found, for *t*-BuHgCl in CH_3CN, δ 1.53 and $J = 260$ Hz. It is apparent in our reactions, though, that none of the $t\text{-}BuHg^+$ survived even the 2:1 oxidations (Table II, runs 5, 7, and 8). Had that happened, conversion into *t*-BuHgCl would have followed on injection of 4 M LiCl. It is seen that, in contrast, $MeHg^+$, $EtHg^+$, and $BuHg^+$ do survive in 2:1-level oxidations, to be converted into the corresponding RHgCl for assay by GC (Tables I and III).

It is arguable, however, that if $t\text{-}Bu^+$ was present as *t*-BuHgCl in Kochi's 2:1 oxidations, it must have been *t*-BuHgCl that was oxidized in the 4:1 oxidation levels.[4] We have found that *t*-BuHgCl is, in fact, oxidized by $Th^{\bullet+}ClO_4^-$ in CH_3CN solution and almost all of the *t*-Bu groups ended as products of reaction of $t\text{-}Bu^+$, namely, isobutene, *t*-BuOH, and *t*-BuNHAc. Analogously, $PhCH_2HgCl$ was readily oxidized by $Th^{\bullet+}ClO_4^-$ in CH_2Cl_2, with the formation of $PhCH_2Cl$ (65.4%) and benzylthianthrenes (totaling 26.7%). Formation of the last products suggests that benzyl radicals were formed and were trapped at the ring positions of $Th^{\bullet+}$. 5-Benzylthianthrenium perchlorate (**1f**) was not obtained, but this is not surprising because chloride ion not only was present in solution but was also added immediately after reaction ended. Had **1f** been formed, reaction with Cl^- would have ensued. At the same time, it is possible that oxidation of benzyl radical occurred rather than trapping at the sulfur atom and that benzyl cation was trapped by Cl^-. Last in these reactions of RHgCl with $Th^{\bullet+}ClO_4^-$ we note that although each involved the 2:1 ratio of $Th^{\bullet+}ClO_4^-$/RHgCl, only the reaction with $PhCH_2HgCl$ gave an almost quantitative yield of HgO after workup. In contrast, reaction with *t*-BuHgCl gave Hg_2Cl_2 as the major (58.4%) and HgO (40%) as the minor product. We are not able to account for the difference. Results are summarized in Table V.

In these connections we can comment here on the difference in practice of our earlier[2] and present work. Earlier, we used 1% (i.e., 0.25 M) aqueous LiCl to convert RHg^+ into RHgCl. The concentration of Cl^- was low enough to allow sulfonium ions to survive as the perchlorates (**1**). In the present work, use of 4 M LiCl converted RHg^+ into RHgCl and also displaced R from sulfonium ions as RCl.

The Argument for Electron Transfer. The basis for diagnosis of electron transfer rather than of direct electrophilic displacement in the reactions of MeHgR with $Th^{\bullet+}ClO_4^-$ was Kochi's findings in reactions of $IrCl_6^{2-}$. Now, oxidation of organometals by $IrCl_6^{2-}$ occurs by inner-sphere electron transfer.[5,6] We do not mean to imply, though, in arriving at the diagnosis of electron transfer that oxidations by $Th^{\bullet+}ClO_4^-$ are of the inner-sphere type. Inner-sphere electron transfer from organometals to $IrCl_6^{2-}$ is characterized by selectivity in radical formation. The selectivity of forming $Et^\bullet$ over $Me^\bullet$ is approximately 11-fold. Outer-sphere electron-transfer oxidation of the same organometals has even greater selectivity, being of the order of 26-fold for ethyl over methyl.[5,6] Therefore, our results rule out cleavage of an alkyl–mercury bond by electrophilic displacement but do not distinguish between inner- and outer-sphere electron transfer. There is no compelling reason to favor the former. We have assumed that outer-sphere electron transfer occurs in analogy with reactions of bulky tris(1,10-phenanthroline)iron(III) oxidants[5] and have calculated $(\Delta G^{\ddagger})^{1/2}$ for the electron transfer according to the Marcus equation as delineated by Kochi and co-workers[5] and described in the Experimental Section. The results are given in Table VI in

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Table VI. Comparison of $(\Delta G^{\ddagger})^{1/2}$ for Electron Transfer between R_2Hg and the Oxidants $Fe(phenanthroline)_3^{3+}$ and $Th^{\bullet +}ClO_4^{-}$ [a]

	$(\Delta G^{\ddagger})^{1/2}$, kcal/mol	
R_2Hg	$Fe(phen)_3^{3+}$ [b]	$Th^{\bullet +}ClO_4^-$
Me_2Hg	4.08	3.67
Et_2Hg	3.20	2.84
Bu_2Hg	3.11	2.75
$(PhCH_2)_2Hg$	2.46	2.14
t-Bu_2Hg	2.32	2.00
MeHgEt	3.59	3.21
MeHg-*i*-Pr	3.23	2.87
MeHg-*t*-Bu	3.05	2.70

[a] Details about calculations are given in the Experimental Section. [b] Reference 5.

comparison with $(\Delta G^{\ddagger})^{1/2}$ for oxidation by $(phen)_3Fe^{III}$ itself. The activation parameters for the two oxidants in the series of R_2Hg are quite close, in spite of the sizeable difference in oxidation potentials of relevant couples, namely, 1.212 V for $(phen)_3Fe^{III}$ and 1.54 for $Th^{\bullet +}$ vs NHE. The difference in oxidation potentials is offset by the difference in assumed reorganization energies, namely 0 and 10 kcal/mol, respectively.

Experimental Section

Gas chromatographic (GC) analyses were made on a Varian gas chromatograph, Model 3700, attached to a Spectra-Physics integrator, Model 4290. The following columns were used: A, 13-ft, $^1/_8$-in. stainless steel (ss), 20% BEEA on Chrom PAW 60–80 mesh, with an 8-in. similar guard column, for hydrocarbon gases; B, 6-ft, $^1/_8$-in. ss, 10% Carbowax on Chrom WHP 80–100 mesh, with a 6-in. similar guard column, for reasonably volatile products; C, 1.5-ft, $^1/_8$-in. ss, 5% OV-101 on Chrom WHP 100–120 mesh, and D, 8-ft, $^1/_8$-in. ss, 10% OV-101 on Chrom WHP 80–100 mesh for less volatile solid products; E, 6-ft, $^1/_8$-in. ss, 5% SE-30 on Supelcoport 100–200 mesh; F, 7-ft, 3-mm glass, 20% BEEA on Chrom PAW 60–80 mesh. The columns were used isothermally or with programmed heating as necessary. Cyclohexane and 2,3-dimethylbutane were used as internal standards for analyses on columns A and B, while naphthalene was used analogously for columns C, D, and E. In some analyses on columns C, D, and F a concentration factor (CF) was measured immediately prior to analysis for each component of the mixture being analyzed, instead of using an internal standard. Qualitative thin-layer chromatography (TLC) was carried out on Kodak chromatogram silica gel sheets, whereas quantitative, preparative-scale TLC (PTLC) was carried out on 2-mm silica gel plates from either E. Merck (no. 5766, 60F254) or Analtech (Uniplates GF). Mass spectra (MS) were obtained with a Hewlett-Packard Model 5995 instrument, either in the GC–MS or selected-ion-monitoring (SIM) mode. ^1H and ^{13}C NMR were recorded on IBM-Bruker instruments at 200- and 300-MHz fields. Chemical shifts (δ) are in ppm with respect to TMS and coupling constants (J) are in hertz.

Acetonitrile (CH_3CN, Eastman Chemicals 488) was distilled over P_2O_5 and stored under argon. Tetrahydrofuran (THF, Fisher T397-4) was distilled over $LiAlH_4$ and stored under argon. Dichloromethane (CH_2Cl_2, Omnisolve) was used as obtained. Alkylmagnesium chlorides (RMgCl, R = Me, Et, *i*-Pr, *t*-Bu, Bu) were obtained as 2 or 3 M solutions in THF from Aldrich Chemical Co. Hydrocarbon gases (ethane, ethene, propane, propene, butane, butene, isobutane, isobutene) were from Matheson, Coleman and Bell. Almost all other common chemicals for preparative and analytical work were from Aldrich. Thianthrene (Th) was from Fluka AG and was purified by chromatography on silica gel with petroleum ether before crystallizing from acetone, mp 155–156 °C.

Dimethylmercury (Me_2Hg) was from Alfa, diethylmercury (Et_2Hg) was from Pfalz and Bauer, and dibenzylmercury was from Strem. Me_2Hg and Et_2Hg were distilled before use. All other dialkylmercurials (R_2Hg and MeHgR) except diallylmercury were prepared by addition of an excess (50%) of the Grignard reagent in THF to a solution of the alkylmercuric chloride in a mixture of ether and THF. For the unsymmetrical MeHgR, MeMgCl was added to the appropriate RHgCl.[12] Products were either distilled under reduced pressure or recrystallized (*t*-Bu_2Hg) after column chromatography. Boiling and melting points agreed with literature values.[13] ^1H NMR ($CDCl_3$): MeHgEt, δ 1.32 (t, 3 H, CH_3CH_2, $J = 8.0$, $J_{Hg-H} = 132.8$), 1.02 (q, 2 H, CH_3CH_2, $J = 8.0$ $J_{Hg-H} = 103.8$), 0.256 (s, 3 H, CH_3, $J_{Hg-H} = 94.7$). MeHg-*i*-Pr, δ 1.39 (m, 7 H, *i*-Pr, $J_{Hg-CH} = 185.3$, $J_{Hg-CH_3} = 125.8$), 0.257 (s, 3 H, CH_3, $J_{Hg-H} = 88.8$). MeHg-*t*-Bu, δ 1.30 (s, 9 H, *t*-Bu, $J_{Hg-H} = 112$) 0.30 (s, 3 H, CH_3, $J_{Hg-H} = 85$). *t*-Bu_2Hg, δ 1.20 (s, *t*-Bu, $J_{Hg-H} = 102.9$). MeHgCl was obtained from Alfa, while all other RHgCl were prepared by addition of RMgCl to a solution of $HgCl_2$ in THF. The products were crystallized from ethanol and had melting points agreeing with those in the literature.[14-16] ^1H NMR ($CDCl_3$): MeHgCl, δ 1.15 (s, 3 H, $J_{Hg-H} = 200.8$). EtHgCl, δ 2.01 (q, 2 H, CH_3CH_2, $J = 7.8$, $J_{Hg-H} = 200.2$), 1.38 (t, 3 H, CH_3CH_2, $J = 7.8$, $J_{Hg-H} = 286$). *i*-PrHgCl, δ 2.63 (sept, 1 H, $J = 7.3$, $J_{Hg-H} = 190$), 1.51 (d, 6 H, $J = 7.3$), $J_{Hg-H} = 284$). *t*-BuHgCl, δ 1.53 (s, $J_{Hg-H} = 260$).

Diallylmercury was prepared by reaction of allylmagnesium bromide, prepared in ether, with $HgBr_2$ in THF.[17] The product had bp 90–92 °C (6.5 Torr) and a 60-MHz ^1H NMR ($CDCl_3$) spectrum corresponding well with that reported earlier.[18]

N-Ethylacetamide ($EtNHCOCH_3$) was obtained from Aldrich. *t*-$BuNHCOCH_3$ was prepared from *t*-BuOH by the Ritter reaction.[19] $PhCH_2NHCOCH_3$[20] and *i*-$PrNHCOCH_3$[21] were prepared by acetylating the corresponding amines. Solids were recrystallized and had satisfactory melting points. Liquid *i*-$PrNHCOCH_3$ was distilled and had bp 105–106 °C (17 Torr).

$Th^{\bullet +}ClO_4^-$ and $Th^{\bullet +}BF_4^-$ were prepared as described earlier.[22,23] *$Th^{\bullet +}ClO_4^-$ is a potential explosive and should be treated carefully.* Our practice is to filter on glass-fiber "paper", avoiding fritted-disk filters and metal spatulas. The product has a longer shelf life than $Th^{\bullet +}BF_4^-$ (which decomposes slowly in an unknown way over periods of months) but should be used soon after preparation.

Reaction of Me_2Hg with $Th^{\bullet +}ClO_4^-$. A solution/suspension of 635 mg (2.01 mmol) of $Th^{\bullet +}ClO_4^-$ in 2.0 mL of CH_3CN was prepared in a septum-capped, argon-filled flask. To the stirred mixture was added dropwise by microsyringe a 1.0 M solution of Me_2Hg in acetonitrile until the color of $Th^{\bullet +}$ was discharged. Addition took 10 min and required 1.0 mL (1.0 mmol) of solution. The solvent was evaporated on a rotary evaporator and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was shaken with 1% aqueous LiCl, separated, concentrated to ca. 5 mL, and diluted with 50 mL of ether, causing the precipitation of 254 mg (0.767 mmol, 76.3% stoichiometric) of 5-methylthianthreniumyl perchlorate (**1a**). The filtrate, after removal of **1a**, was evaporated to give 450 mg of white residue, which was transferred in 3 mL of CH_2Cl_2 to a 25-mL volumetric flask containing naphthalene as a standard. The volume was made up to 25 mL with ether for GC analysis on column E for Th and ThO. Traces of two isomers of methylthianthrene were found by GC–MS but were too small for GC assay. The solution remaining from GC analysis was concentrated to a small volume and used for PTLC. MeHgCl (213 mg, 0.849 mmol, 84.9% stoichiometric) was removed from the plate with CH_2Cl_2, mp 168–170 °C.

The identity of **1a** was confirmed with ^1H NMR ($CDCl_3$/CH_3CN): δ 8.22 (dd, 2 H, H_4), 7.62–7.91 (m, 6 H, $H_{1,2,3}$), 3.22 (s, 3 H, CH_3).

Quantitative data are given in Table III, run 12.

Reactions of MeHgR with $Th^{\bullet +}ClO_4^-$. MeHg-*t*-Bu. Run 1. In a 25-mL septum-capped, argon-filled volumetric flask was

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placed 184 mg (0.583 mmol) of $Th^{\bullet+}ClO_4^-$ and 15 mL of CH_3CN. Neat MeHg-*t*-Bu was added by microsyringe until the stirred mixture was decolorlized, which occurred after the addition of 79.0 mg (0.290 mmol) of MeHg-*t*-Bu. The solution was made of to 25 mL and a 5.0-mL aliquot was removed. To this was added 0.05 mL of aqueous 4 M LiCl, and the solution was analyzed on columns B and C. Results are given in Table I. The solution was then evaporated and the residue was dissolved in 2 mL of CH_2Cl_2. This solution was diluted with 20 mL of ether without formation of a precipitate (**1d**).

MeHg-*i*-Pr. Run 2. The same procedure as above was followed. Cyclohexane was used as the GC standard in the first 5.0-mL aliquot of reaction solution, and analysis was carried out with columns A and B. A second 5.0-mL aliquot was diluted with 25 mL of ether without formation of a precipitate (**1c**). Ten milliliters of this solution was shaken with 25 mL of 1% aqueous LiCl. The ether layer and ether extracts were dried ($MgSO_4$) and evaporated. The residue was dissolved in 10 mL of CH_3CN/CH_2Cl_2 (1:1) for analysis on column C. Results are given in Table I.

MeHg-*i*-Pr. Run 3. A 4:1 molar ratio of $Th^{\bullet+}ClO_4^-$/MeHg-*i*-Pr was used, as described above, in 10 mL of CH_3CN. After being stirred overnight, unused $Th^{\bullet+}ClO_4^-$ in the mixture was quenched by addition of 0.5 mL of water. Workup and GC analyses (columns A, B, and C) gave the results listed in Table I.

MeHgEt. Run 4. Reaction was carried out as in run 1, and results are given in Table I.

Formation of 1-RTh, 2-RTh, and R_2Th. These products are listed in runs 2–4 in Table I. The products were identified with GC–MS as substituted thianthrenes. Several GC peaks were obtained for isomers of R_2Th, and these were integrated collectively. Assay by GC was made on the basis that these products would have the same response factor as Th.

Reactions of *t*-Bu_2Hg. With $Th^{\bullet+}ClO_4^-$, Molar Ratio 2:1. Run 5. To a stirred solution/suspension of 319 mg (1.01 mmol) of $Th^{\bullet+}ClO_4^-$ in 3.0 mL of CH_3CN was added in one portion by syringe a solution of 160 mg (0.509 mmol) of *t*-Bu_2Hg in 5.0 mL of CH_3CN. The color of $Th^{\bullet+}$ was discharged immediately, and a grayish white precipitate appeared in the yellow solution. Addition of 0.10 mL of 4 M LiCl discharged the yellow color but the precipitate remained unchanged. To the flask were added 12.0 mL of ether and 0.10 mL of 4 M aqueous K_2CO_3. Part of the precipitate dissolved, while the remainder became more gray. Ten milliliters of the supernatant was removed to a volumetric flask containing the standard, naphthalene, and was analyzed on columns A, B, and D. The results are given in Table II. It was not possible to assay *t*-$BuNHCOCH_3$ reliably by GC. Therefore, the remaining 10 mL of reaction mixture was filtered and the filtrate was chromatographed on a column of silica gel (Baker, 40 μm) with CH_2Cl_2 to remove Th, mp 154–156 °C, and CH_2Cl_2/MeOH (1:1) to remove *t*-$BuNHCOCH_3$, mp 95.5–96.5 °C. The filtered, gray solid was triturated with cold concentrated HNO_3 and again removed by filtration. The residue (109 mg, 0.231 mmol) had mp 397 °C (sublimed) and was evidently Hg_2Cl_2. The filtrate of nitric acid was made alkaline with NaOH without formation of a precipitate of HgO. All results are listed in Table II.

With $Th^{\bullet+}ClO_4^-$, Molar Ratio 4:1. Run 6. To a solution of 320 mg (1.02 mmol) of $Th^{\bullet+}ClO_4^-$ in 10 mL of CH_3CN in a septum-capped, argon-filled volumetric flask was added a solution of 79.9 mg (0.254 mmol) of *t*-Bu_2Hg in 10 mL of CH_3CN. Reaction was rapid with the formation of a yellow solution and yellow precipitate. The flask was made up to volume with CH_3CN, and two 5.0-mL aliquots of the supernatant solution were withdrawn. One of these was transferred to a septum-capped volumetric flash containing 2,3-dimethylbutane as standard. To this solution was added 0.05 mL of 4 M LiCl, and the solution was analyzed on column B for isobutane, isobutene, *t*-BuCl, and *t*-BuOH. To the remaining yellow reaction mixture (15 mL) was added to 10 mL of ether. The yellow solid was removed by filtration to give 142 mg (0.135 mmol) of **2**, mp 276–278 °C. The filtrate was shaken with 10 mL of 1% LiCl, and the organic layer and ether washings were worked up to give a solid residue. The residue was dissolved in a small volume of CH_2Cl_2 for assay of Th, ThO, and *t*-BuNHAc by PTLC. The aqueous layer contained an insoluble solid, which was removed by filtration. The solid was insoluble in cold concentrated HNO_3 and was assumed to be Hg_2Cl_2. The filtrate of HNO_3 was made alkaline with NaOH, giving a yellow precipitate of HgO. All results are given in Table II.

With $Th^{\bullet+}BF_4^-$, Molar Ratio 2:1. Run 7. To a solution/suspension of 306 mg (1.01 mmol) of $Th^{\bullet+}BF_4^-$ in 2.0 mL of CH_3CN under the usual conditions was added a solution of 161 mg (0.505 mmol) of *t*-Bu_2Hg in 5.0 mL of CH_3CN. When half the solution had been added, the purple color of $Th^{\bullet+}$ had disappeared and the solution was yellow. However, on completion of the addition the solution became colorless and a gray precipitate along with metallic Hg had formed. Following the addition of *t*-Bu_2Hg 0.10 mL of 4 M LiCl was injected, followed by enough ether to make 20 mL and 0.10 mL of 4 M K_2CO_3, causing part of the precipitate to dissolve. Ten milliliters of the supernatant solution was removed for GC analysis on columns A, B, and D. The remaining supernatant was decanted. The residue of gray precipitate and Hg was washed with water and the residue was treated with concentrated HNO_3. The insoluble solid was filtered, washed, and dried to give 10.8 mg (0.0229 mmol) of Hg_2Cl_2. The nitric acid solution was tested for Hg^{2+} with KI and gave a red-orange precipitate of HgI_2, which dissolved in an excess of KI. The nitric acid solution was made alkaline with NaOH and gave a precipitate of 101 mg (0.467 mmol) of HgO. The unused portion (7 mL) of the original reaction solution and washings was evaporated and assayed for Th, ThO, and *t*-$BuNHCOCH_3$ by PTLC. All results are given in Table II.

With $Th^{\bullet+}BF_4^-$, Molar Ratio 2:1. Run 8. Reaction was carried out as in run 7 but with 212 mg (0.700 mmol) of $Th^{\bullet+}BF_4^-$ and 111 mg (0.351 mmol) of *t*-Bu_2Hg in a septum-capped 10-mL volumetric flask. Immediately after addition of the *t*-Bu_2Hg solution, 0.10-mL portions of 4 M LiCl and 4 M K_2CO_3 were injected. Results of GC analysis of the supernatant solution on columns A, B, and C are given in Table II. The precipitate of Hg_2Cl_2 and Hg was treated as in run 7.

Reaction of Diallylmercury with $Th^{\bullet+}ClO_4^-$. Run 11. A solution of 1.00 g (3.2 mmol) of $Th^{\bullet+}ClO_4^-$ in 20 mL of CH_3CN was prepared under argon in a septum-capped flask. To the stirred solution was added dropwise by syringe through the septum over a period of 30 min a solution of 226 mg (0.79 mmol) of diallylmercury in 5 mL of CH_3CN. The color of $Th^{\bullet+}$ disappeared at the end of the addition, during which a yellow precipitate had formed. The solution was stirred for 5 h and filtered, giving 428 mg (0.409 mmol) of **2**. The filtrate was evaporated in a rotary evaporator, and to the residue were added 1.0 mL of D_2O and 10 mL of CH_2Cl_2. ^1H NMR failed to show the presence of organic products in the separated D_2O layer. The CH_2Cl_2 solution was shaken with aqueous $NaHCO_3$, and the layers were separated. Treatment of the $NaHCO_3$ layer with 6 N HCl gave 86.2 mg of gray precipitate, assumed to be Hg_2Cl_2. The acidic filtrate, after removal of Hg_2Cl_2, was made alkaline with NaOH; a precipitate of HgO was not obtained. The dried ($MgSO_4$) CH_2Cl_2 layer was made up to 50 mL with CH_2Cl_2. A 5-mL aliquot of this solution was removed for analysis by GC–MS and GC with biphenyl as an internal standard. Th, ThO, and 1- and 2-allylthianthrene were present and were assayed. The allylthianthrenes were assumed to have the same response factor as Th. The remaining 45 mL of the CH_2Cl_2 solution was evaporated to a small volume. To the residue were added 10 mL of CH_2Cl_2 and 30 mL of dry ether. A precipitate formed and was removed by filtration to give 398 mg of 5-allylthianthrenium perchlorate (**1g**), mp 110–112 °C. This represents a total yield of 442 mg (1.24 mmol) of **1g**. The product had a strong ClO_4^- band at 1090 cm^{-1}. The CH_2Cl_2–ether filtrate was evaporated on a rotary evaporator, giving a solid residue. The residue was taken up in a small volume of CH_2Cl_2, and the solution was streaked on a TLC plate. Development with CH_2Cl_2 gave two bands, the upper one of which gave, after extraction with CH_2Cl_2, 128 mg of Th, representing a total yield of 142 mg (0.658 mmol) of Th. The small lower band was discarded. The summary of products and yields is given in Table II.

5-Allylthianthrenium perchlorate (**1g**) decomposed in $(CD_3)_2SO$ to give the ^1H NMR spectrum of Th and the allyl group. ^1H NMR data were obtained without decomposition in CD_3Cl, δ 8.044 (dd, 2 H, H_4, $J_{4,3} = 7.92$, $J_{4,2} = 1.45$), 7.955 (dd, 2 H, H_1, $J_{1,2} = 7.93$, $J_{1,3} = 1.41$), 7.825 (dt, 2 H, H_2, $J_{2,(1,3)} = 7.63$, $J_{2,4} = 1.51$), 7.688

(dt, 2 H, H_3, $J_{3,(2,4)}$ = 7.64, $J_{3,1}$ = 1.46), 5.768 (m, 1 H), 5.412 (d, 1H, H_{cis}, J = 9.88), 5.168 (dt, 1 H, H_{trans}, J = 15.88 and 0.95), 4.347 (dd, 2 H, CH_2, J = 7.65 and 0.89).

Product **2** was washed with ether and dried and had mp 275–278 °C dec. Anal. Calcd for $C_{36}H_{24}HgS_2Cl_2O_8$: C, 41.3; H, 2.31; S, 18.3; Cl, 6.77. Found: C, 41.2, 41.1; H, 2.18, 2.18; S, 18.5, 18.4; Cl, 6.3, 6.3.

Reactions of $(PhCH_2)Hg$ with $Th^{\bullet+}ClO_4^-$. Run 9. To a suspension of 1.26 g (4.00 mmol) of $Th^{\bullet+}ClO_4^-$ in 8.0 mL of CH_3CN was added dropwise by microsyringe a 0.50 M solution of $(PhCH_2)_2Hg$ in CH_2Cl_2. The color of $Th^{\bullet+}$ was discharged after addition of 2.05 mL, corresponding with 1.025 mmol of $(PhCH_2)_2Hg$. Next was added 1.0 mL of 2.5 M aqueous K_2CO_3 and, after 2 min of stirring, 200 mg of LiCl. The mixture was stirred for 10 min and next diluted with 10 mL of CH_2Cl_2 for direct GC analysis on column C. The products found were $PhCH_2OH$, $PhCH_2Cl$, $PhCH_2NHCOCH_3$, $(PhCH_2)_2$, Th, and ThO. At higher retention times were found peaks assignable on the basis of GC–MS to 1-$PhCH_2Th$ and 2-$PhCH_2Th$ (M^+, *m/z* 306, 90%) and several small peaks, all assignable by GC–MS to $(PhCH_2)_2Th$ (M^+, *m/z* 396, 100%). Quantitative results are given in Table II. After GC analysis the solvent was removed on a rotary evaporator and the solid residue was treated with 25 mL of 2 N NaOH, causing a yellow precipitate to form. Organic material was dissolved by adding 5 mL of CH_2Cl_2. The yellow precipitate was filtered, washed, and dried to give 213 mg (0.983 mmol, 96%) of (assumed) HgO.

Run 10. Isolation of 2. A solution of 60.1 mg of $(PhCH_2)_2Hg$ in 5 mL of CH_3CN was added by syringe to 198 mg (0.628 mmol) of $Th^{\bullet+}ClO_4^-$ in a septum-capped, argon-filled flask. The color of $Th^{\bullet+}$ disappeared and a yellow precipitate formed in the yellow solution. The precipitate was removed and washed with ether to give 63.5 mg (0.0606 mmol) of **2**, mp 268–270 °C. The ether washings were added to the yellow filtrate, causing the precipitation of 77.0 mg (0.0734 mmol) of **2**, mp 267–270 °C. The filtrate was partially evaporated on a rotary evaporator and to it was added 0.10 mL of 4 M LiCl and 43.8 mg of the internal standard, naphthalene. A small amount of white solid formed. GC analysis of the supernatant solution was carried out on column C and gave the results listed in Table II.

Treatment of 2 with LiCl. To a suspension of 30.8 mg (0.0294 mmol) of **2** in 5 mL of CH_3CN was added 0.05 mL of 4 M LiCl. The yellow solid decomposed and the color of the solution was discharged. Naphthalene was added as an internal standard and GC analysis was carried out on column C, giving 0.084 mmol (95.6%) of Th, 0.0005 mmol (0.6%) of 1-$PhCH_2Th$, and 0.0022 mmol (2.5%) of 2-$PhCH_2Th$. No trace of peaks corresponding with $PhCH_2Cl$, $PhCH_2OH$, $PhCH_2NHCOCH_3$, and $(PhCH_2)_2$ was found.

Reaction of MeHgEt and Et_2Hg with $Th^{\bullet+}ClO_4^-$. Isolation of 1b. MeHgEt. A solution of 166 mg (0.526 mmol) of $Th^{\bullet+}ClO_4^-$ in 20 mL of CH_3CN was prepared under argon in a 50-mL, septum-capped flask. To the stirred solution was added 64.4 mg (0.263 mmol) of MeHgEt by microsyringe. The color of $Th^{\bullet+}$ disappeared immediately. After 10 min of stirring the solvent was removed at 30 °C. The residue was dissolved in 10 mL of CH_2Cl_2, and the solution was shaken with 50 mL of 1% (0.235 M) aqueous LiCl. The layers were separated and the aqueous layer was extracted with 3 × 10 mL of CH_2Cl_2. The dried ($MgSO_4$) CH_2Cl_2 solution was evaporated to about 5 mL and diluted with 50 mL of ether. 5-Ethylthianthrenium perchlorate (**1b**) precipitated. Filtration and washing with ether gave 52.1 mg (0.155 mmol), 59% based on MeHgEt, of crude **1b**, mp 120–121 °C dec; lit.[2] mp 133–135 °C. ^1H NMR ($CDCl_3$) showed the spectrum of **1b** along with smaller signals from an ethylthianthrene. A 26.8-mg (0.0777 mmol) sample of the crude **1b** was placed in a septum-capped volumetric flask and 10 mL of CH_3CN containing known amounts of two internal standards, cyclohexane and naphthalene. Aqueous 4 M LiCl (0.03 mL) was injected through the septum by microsyringe and the solution, after shaking, was used directly for GC analysis. Use of column A gave 0.0724 mmol (93.3%) of EtCl, use of column C gave 0.0727 mmol (93.5%) of Th and 0.005 mmol (6.4%) of the two ethhylthianthrenes, and use of column B showed that ethanol was absent.

Et_2Hg. Similarly, reaction of 167 mg (0.530 mmol) of $Th^{\bullet+}ClO_4^-$ with 68.6 mg (0.265 mmol) of Et_2Hg was carried out. Workup gave 53.1 mg (0.154 mmol, 58% based on Et_2Hg) of crude **1b**, mp 118–120 °C. Reaction of the crude **1b** with 4 M LiCl gave 91% of EtCl, 88.6% of Th, and 9.3% of ethylthianthrenes.

A sample of **1b** from the reaction of MeHgEt was purified by reprecipitation from CH_2Cl_2 with ether until signals from EtTh were no longer discernible by ^1H NMR. ^1H NMR ($CDCl_3$), 300 MHz, δ 8.284 (dd, 2 H, H_4, J = 7.81 and (av) 1.24), 7.860 (dd, 2 H, H_1, J = 7.87 and (av) 1.50), 7.788 (td, 2 H, H_2, J = 7.35, 7.89, and (av) 1.44), 7.689 (td, 2 H, H_3, J = 7.62, 7.56, and (av) 1.53). Second-order splittings of 0.33–0.47 Hz were seen in the smaller doublets of some signals from H_1 and H_4. Similar splitting (0.40 Hz) was seen in the central peaks of the H_3 triplet. ^{13}C NMR ($CDCl_3$), 300 MHz, δ 9.1 (CH_3), 36.256 (CH_2), 116.820, 129.947, 130.111, 134.631, 134.811, and 135.695 (ring carbons).

Reaction of Bu_2Hg with $Th^{\bullet+}ClO_4^-$. Run 14. To a stirred solution/suspension of 790 mg (2.5 mmol) of $Th^{\bullet+}ClO_4^-$ in 5.0 mL of CH_3CN under argon was added 1.77 mL (1.0 mmol) of a 0.564 M solution of Bu_2Hg in CH_3CN/CH_2Cl_2 (1:1). After 2 min of stirring, the excess of $Th^{\bullet+}ClO_4^-$ was quenched by injecting 0.50 mL of 2.5 M K_2CO_3, and 500 mg of LiCl was then added. Stirring was continued for 24 h, after which the solution was made up to volume with CH_2Cl_2 and anayzed by GC on columns C and D.

Run 15. Isolation of Products. The same procedure as in run 14 was used except that addition of LiCl was omitted. Following the addition of K_2CO_3, 20 mL of CH_2Cl_2 was added and the phases were separated. The aqueous phase was extracted with 4 × 10 mL of CH_2Cl_2. The collected CH_2Cl_2 solution was dried and worked up to give 920 mg of white solid. This was dissolved in a small volume of CH_2Cl_2 and separated into four broad bands by PTLC. The uppermost band was extracted with 250 mL of CH_2Cl_2 to give 354 mg of solid that was found by GC on columns C and D to contain (in mmol) BuHgCl (0.025), Th (1.53), 1-BuTh (0.011), 2-BuTh (0.021), and a mixture of Bu_2Th (0.0065). The second band was extracted with CH_2Cl_2 and gave 66 mg of solid consisting (mmol) of ThO (0.242), Th (0.016), and Bu_2Th (0.002). The third band, known from previous work to correspond with 5-butylthianthrenium perchlorate (**1e**) was extracted first with 250 mL of CH_2Cl_2 and next with 100 mL of CH_2Cl_2/acetone (5:1). These extracts yielded 297 mg of an oil that was dissolved in 5.0 mL of CH_3CN to which was next added 200 mg of LiCl. The mixture was stirred for 24 h, after which 5.0 mL of CH_2Cl_2 was added to dissolve Th that had formed. Analysis on columns C and D gave (in mmol) BuCl (0.695), BuHgCl (0.046), Th (0.536), 1-BuTh (0.013), 2-BuTh (0.090), and mixed Bu_2Th (0.018). The last PTLC band, at the origin, was extracted with 75 mL of acetone. The extract was stirred with 1 g of LiCl for 30 min, filtered, and evaporated, giving a solid residue. This was extracted with 3 × 10 mL of CH_2Cl_2 to give 254 mg of solid. Analysis by GC gave (in mmol) BuHgCl (0.893), Th (0.025), and ThO (0.003). All data are summaried in Table III.

Reaction of $PhCH_2HgCl$ with $Th^{\bullet+}ClO_4^-$. A 0.50-M solution of $PhCH_2HgCl$ in CH_2Cl_2 was added dropwise in the usual way to a solution of 732 mg (2.0 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of CH_2Cl_2. Discharge of the $Th^{\bullet+}$ color required 2.0 mL (1.0 mmol) of $PhCH_2HgCl$ solution. Immediately, 200 mg of LiCl was added and was followed 5 min later with 1.0 mL of K_2CO_3 solution, resulting in formation of a yellow-brown solid. Analysis of the supernatant solution on column C gave the products listed in Table V. Filtration of the solution gave 201 mg (0.928 mmol, 93%) of HgO.

Reaction of *t*-BuHgCl with $Th^{\bullet+}ClO_4^-$. A solution of 92.5 mg (0.315 mmol) of *t*-BuHgCl in 8 mL of CH_3CN was injected into a flask containing a stirred suspension of 199 mg (0.631 mmol) of $Th^{\bullet+}ClO_4^-$ in 2 mL of CH_3CN. The color of $Th^{\bullet+}$ disappeared after 10 min and a white precipitate formed. A 5-mL portion of the light orange supernatant solution was withdrawn, and to it were added a weighed amount of naphthalene, 0.02 mL of 4 M LiCl, and 0.02 mL of 4 M K_2CO_3. The color of the solution was discharged. The solution was then made up to 25 mL with CH_3CN. GC analysis on column C gave 0.219 mmol (69.5%) of *t*-BuNHAc, 0.603 mmol (95.6%) of Th, and 0.023 mmol (3.6%) of ThO. GC analysis on column B gave 0.034 mmol (10.8%) of isobutene and 0.54 mmol (17.1%) of *t*-BuOH.

The white precipitate that had been formed in the initial reaction was removed, washed with MeOH, and dried, to give 43.4

mg (0.092 mmol) of Hg_2Cl_2, mp 386–394 °C. This represents 58.4% of the Hg content of the *t*-BuHgCl. The filtrate from the Hg_2Cl_2 was evaporated. The residue was treated with 10 mL of 1.0 M HNO_3, and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed with water, and the washings were combined with the nitric acid solution. This solution was made alkaline with 1.0 M NaOH. A yellow-orange precipitate formed, which was isolated and washed with MeOH by centrifugation to give 20.5 mg of HgO, representing a total yield of 34.2 mg (0.126 mmol, 40%). Heating at 450 °C caused the formation of metallic Hg. The summation of products, therefore, accounted for 99.2% of the $Th^{\bullet+}ClO_4^-$, 97.5% of the *t*-Bu groups, and 98.4% of the Hg in the *t*-BuHgCl.

Reactions of $Th^{\bullet+}ClO_4^-$ with Hg. (A) Excess of Hg. A mixture of 4.04 g (20.14 mmol) of Hg, 600 mg (1.90 mmol) of $Th^{\bullet+}ClO_4^-$, and 9 mL of CH_3CN was sealed under argon in a glass ampule, which was placed in a sonic bath at 20 °C. The $Th^{\bullet+}$ color disappeared within 2 min. The mixture contained a yellow precipitate. The ampule was opened and to it were added 16 mL of CH_2Cl_2 and 1 mL of water. GC analysis of the organic phase showed only Th to be present. The two phases were separated, the aqueous phase was washed with CH_2Cl_2, and the combined CH_2Cl_2 solution was washed with 10 mL of water, dried over Na_2SO_4, and evaporated to give 413 mg (1.91 mmol, 100%) of Th. Metallic Hg was recovered by decantation and washing with water and MeOH, giving 3.67 g (18.3 mmol) and signifying the loss by reaction of 1.84 mmol. To the collected water phase was added 0.5 mL of 6 N HCl. A white precipitate formed, which was washed well with water and 2 mL of methanol and dried to give 414 mg (0.877 mmol, 92%) of Hg_2Cl_2. HgO did not form when the aqueous filtrate was made alkaline with NaOH.

(B) Molar Ratio of Reactants 2:1. Reaction was repeated with 206 mg (1.027 mmol) of Hg, 648 mg (2.054 mmol) of $Th^{\bullet+}ClO_4^-$, and 8 mL of CH_3CN. Sonification for 15 min was required for almost all of the $Th^{\bullet+}$ to disappear. After 30 min the color of the mixture was yellow with a yellow precipitate.

Proceeding as earlier, the organic phase, in which GC showed the presence of only Th and ThO, was washed with 3 × 10 mL of water and evaporated. The residue was separated by PTLC into 439 mg (2.03 mmol, 98.8%) of Th and 6.0 mg (0.026 mmol, 1.3%) of ThO. Acidification of the aqueous solution with 6 N HCl gave 25 mg (0.053 mmol, 10.3%) of Hg_2Cl_2. The aqueous filtrate was concentrated under vacuum to remove residual organic solvent and was made alkaline with 25 mL of 5 N NaOH, causing the precipitation of 142 mg (0.66 mmol, 64.3%) of HgO.

Direct Formation of $Th_3Hg(ClO_4)_2$ (2) from $Hg(ClO_4)_2 \cdot 3H_2O$. A weighed portion of $Hg(ClO_4)_2 \cdot 3H_2O$ was shaken with 20 mL of CH_3CN. The solution was filtered and dried over $MgSO_4$ for 3 h. The insoluble portion was dried and weighed and showed that the solution had contained 566 mg (1.25 mmol) of $Hg(ClO_4)_2 \cdot 3H_2O$.

Thianthrene (758 mg, 3.5 mmol) was suspended in the solution, which then became yellow, and the suspension was placed in the sonic bath. The thianthrene dissolved and after 30 min 784 mg of yellow precipitate was formed and was recovered. After a further 60 min, the solution deposited more yellow solid, amounting to a total of 823 mg, mp 275–277 °C. Ether was added to the filtrate but failed to produce more precipitate. The filtrate was assayed by GC and was found to contain 1.15 mmol of Th. On the basis that 2 has the formula $Th_3Hg(ClO_4)_2$, 823 mg (0.785 mmol) contains 2.36 mmol of Th. The account of Th is then 3.51 mmol, namely, 100% of that which was used.

Decomposition of 2 with Water. Assay of Products. A portion (275 mg, 0.262 mmol) of 2 was suspended in 10 mL of water in a separatory funnel and was shaken until all of the yellow solid had disappeared and had been replaced by a precipitate of Th. The Th was extracted with 25 mL of ether. The ether layer was assayed on column C, after addition of 71 mg of naphthalene, which showed that 168.5 mg (0.780 mmol) of Th was present. This represents 99.2% of the anticipated Th content. The ether layer was washed with water, dried, and evaporated to give 237 mg of solid, representing 166 mg (97.6% of theory) of Th and 71 mg of added internal standard. The combined aqueous layer (16 mL) was divided into two equal portions. Addition of 6 N HCl to one portion failed to produce a precipitate. Addition of NaOH to the second portion gave a yellow-orange precipitate. This was recovered by centrifugation and was washed twice with MeOH, giving 56 mg (0.259 mmol, 98.9% of theory) of HgO, decomposing into Hg at 500 °C.

Calculations of $(\Delta G^{\ddagger})^{1/2}$ for Electron Transfer. Values of $(\Delta G^{\ddagger})^{1/2}$ were calculated from the equation $(\Delta G^{\ddagger})^{1/2} = \lambda^{1/2}/2 + F/2\lambda^{1/2}[(E^{\circ}_{RM} + Wp/F) - (E^{\circ}_{ox})]$ given in ref 5. The reorganization energy, λ = 41 kcal/mol, was used for electron transfer between all RM and $Fe(phen)_3^{3+}$, as described by Fukuzumi et al. The value of λ for the couple $Th^{\bullet+}/Th$ was assumed to be ca. 10 kcal/mol,[24] so that λ for this series became 46 kcal/mol. Some values of the term $(E^{\circ}_{RM} + Wp/F)$ had already been tabulated,[5] but those that were not available were calculated from the relationship $\Delta(IP)/\Delta(E^{\circ}_{RM} + Wp/F) = 1.802$, in which $\Delta(IP)$ is the difference between the first ionization potential of Me_2Hg and that of RM, and $\Delta(E^{\circ}_{RM} + Wp/F)$ is the difference between that term for Me_2Hg and the term needed for RM. The relationship was developed from values of IP and $(E^{\circ}_{RM} + Wp/F)$.[5] The IP needed for these calculations were already reported,[25] except that for $(PhCH_2)_2Hg$ (7.70 eV), which was measured for us.[26] Calculated values (in V) of $(E^{\circ}_{RM} + Wp/F)$ were then 1.16 for Bu_2Hg and 0.80 for $(PhCH_2)_2Hg$. The term E°_{ox} in the equation for $(\Delta G^{\ddagger})^{1/2}$ refers to the oxidation potential vs NHE of the oxidant, which for $Fe(phen)_3^{3+}$ is 1.212 V[5] and the $Th^{\bullet+}$ was calculated to be 1.54 V from literature values vs SCE.

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Registry No. **1a**, 65886-47-7; **1b**, 65886-49-9; **1e**, 110547-52-9; **1g**, 105623-15-2; **2**, 125926-51-4; Th, 92-85-3; MeHgEt, 29138-86-1; MeHg-*i*-Pr, 29138-88-3; MeHg-*t*-Bu, 59049-78-4; $Th^{\bullet+}ClO_4^-$, 35787-71-4; $(t\text{-}Bu)_2Hg$, 23587-90-8; $(PhCH_2)_2Hg$, 780-24-5; $(allyl)_2Hg$, 2097-71-4; $Th^{\bullet+}BF_4^-$, 60896-34-6; Me_2Hg, 593-74-8; Et_2Hg, 627-44-1; Bu_2Hg, 629-35-6; *t*-$BuNHCOCH_3$, 762-84-5; MeHgCl, 115-09-3; ThO, 2362-50-7; *i*-$PrNHCOCH_3$, 1118-69-0; 1-(*i*-Pr)Th, 125902-62-7; 2-(*i*-Pr)Th, 125902-63-8; $(i\text{-}Pr)_2Th$, 125902-67-2; $EtNHCOCH_3$, 625-50-3; 1-EtTh, 125902-64-9; 2-EtTh, 49820-02-2; Et_2Th, 125902-68-3; Hg_2Cl_2, 10112-91-1; HgO, 21908-53-2; Hg, 7439-97-6; $PhCH_2NHCOCH_3$, 588-46-5; EtHgCl, 107-27-7; BuHgCl, 543-63-5; 1-BuTh, 125902-65-0; 2-BuTh, 125902-66-1; Bu_2Th, 125902-69-4; *t*-BuHgCl, 38442-51-2; $PhCH_2HgCl$, 2117-39-7.

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[26] We thank Prof. Richard Glass for this measurement.