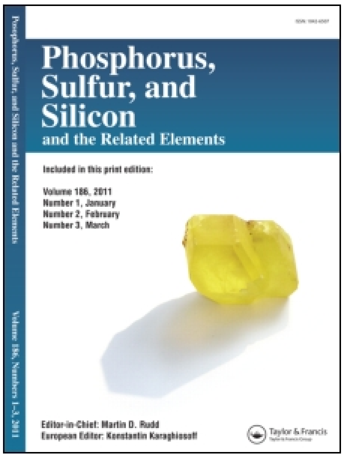

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# Electron-Transfer Reactions of Organosulfur Cation Radicals

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# ELECTRON-TRANSFER REACTIONS OF ORGANOSULFUR CATION RADICALS

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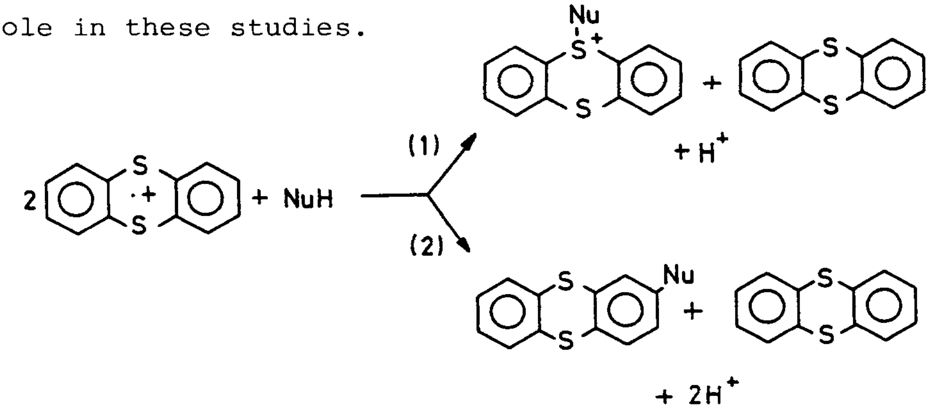
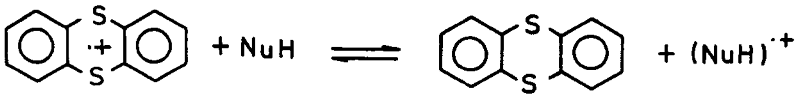
Abstract The thianthrene cation radical ($Th^{\cdot+}$) undergoes electron transfer in reactions with a number of azoalkanes. The oxidized azoalkanes then enter primarily into carbocation reaction pathways rather than the free radical pathways with which they are commonly associated. Examples are given with 1,1'-azoadamantane, phenylazotriphenylmethane, azotoluene, and azo-tertiary-butane. Reactions of $Th^{\cdot+}$ with Grignard agents also result, to varying extents, in electron transfer from the Grignard to $Th^{\cdot+}$. Here again carbocation chemistry is seen but particularly with solvent tetrahydrofuran, which polymerizes. The Grignard group may end up primarily as alkane (e.g., with t-butyl) or may also be trapped by $Th^{\cdot+}$ in the form of a 5-alkylthianthreniumyl ion (e.g. with butyl). Possible mechanisms of reactions are discussed

## INTRODUCTION

Cation-radical chemistry had its beginning in the use of e.s.r. spectroscopy for characterizing newly discovered radical ions, mainly during the 1950s and 1960s. After physical characterization had become more or less commonplace and cation radicals became accepted as being not-so-uncommon reaction intermediates, attention began to turn toward studies of their reactions [3]. Organosulfur cation radicals have played a prominent role in these studies, the reasons for which may be partly historical and partly accidental or coincidental. One-electron oxidation of organosulfur compounds is relatively easy. Relatively stable cation radicals can be made (e.g., for e.s.r. studies) and some of them can be isolated as crystalline salts, such as perchlorates, tetrafluoroborates, hexafluoroantimonates and the like. These characteristics made organosulfur cation radicals available for chemical studies, and particularly the cation radicals of heterocyclics such as thianthrene, phenoxathiin, and phenothiazine. Studies with these cation radicals became all the more attractive as connections became established between the cation radical chemistry and the redox chemistry of the heterocycles and their sulfoxides which had been so well documented decades earlier, particularly in the German literature by Kehrmann and by Pummerer [3j]. Furthermore, unlike the somewhat more limited scope in the chemistry of polynuclear aromatics,the chemistry of organosulfur cation radicals became widened in scope because reactions with nucleophiles led so often to addition at sulfur and occasionally substitution in the rings. Mechanistic studies followed and were adapted particularly well to electrochemical methods especially by Blount, and by Parker [3a]. The thianthrene cation radical ($Th^{\cdot +}$) has had a large role in these studies.





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This paper is devoted mainly to the chemistry of $Th^{\cdot+}$, but not so much to its addition and substitution reactions as to chemistry of other molecules induced by electron transfer to $Th^{\cdot+}$. Addition and substitution in reactions with a nucleophile are represented with eq. 1 and 2. The nucleophile may, of course, be an anion and may also be incapable of losing a proton (e.g., pyridine), calling for changes in these equations. Most of what we know about the chemistry of $Th^{\cdot+}$ and its analogues is reflected in these simple equations. $Th^{\cdot+}$ also undergoes one-electron transfer reactions, represented with eq. 3. In contrast to eq. 1 and 2, this chemistry of $Th^{\cdot+}$ and its analogues has been little studied.

## ELECTRON-TRANSFER REACTIONS

Electron transfer in cation radical chemistry causes reduction of the cation radical. Long-known examples of electron transfer to $Th^{\cdot+}$ and its analogues include reaction with cyanide and halide ions and with trialkylamines. Nothing is known of the fate of the cyano radical and trialkylamine cation radical which should result from the transfer. In the reactions with halide ion it is often thought that electrophilic reaction with halogen follows transfer (eq. 4 and 5), but little has been clarified in these reactions.

$$\mathrm{Th}^{\cdot+} + \mathrm{X}^{-} \rightleftharpoons \mathrm{Th} + 1/2\ \mathrm{X}_2 \tag{4}$$

$$\mathrm{Th} + \mathrm{X}_2 \longrightarrow \text{products} \tag{5}$$

Bromination of N-arylphenothiazines and the reactions of N-arylphenothiazine cation radicals with bromide ion have been studied, however [4]. Reaction with iodide ion (eq. 4) is reversible and in some cases can be carried completely to the cation radical side in the presence of silver ion [3h]. Ring nitration occurs when some organosulfur cation radicals (e.g., phenothiazine $^{\cdot+}$) react with nitrite ion, whereas other nitrite-ion reactions (e.g., with $\mathrm{Th}^{\cdot+}$) lead exclusively to sulfoxide formation. The possibility that electron transfer precedes product formation and that this involves reactions of $\mathrm{NO}_2$ has been discussed but never settled [3h]. Thus, for a long time workers in cation-radical chemistry have encountered electron transfer reactions but the scope of the reactions has not hitherto attracted much attention. This situation has begun to change, however, as this part of cation-radical chemistry becomes caught up in the burgeoning field now being described with the seemingly magical phrase "single electron transfer" and with its initials SET.

Some years ago Parker [5] noted that the reaction of anisole with $\mathrm{Th}^{\cdot+}$ was first order in $\mathrm{Th}^{\cdot+}$ at low and order at high concentrations of $\mathrm{Th}^{\cdot+}$. First order kinetics were explained as resulting from dissociation and escape of $\mathrm{AnH}^{\cdot+}$ from a complex between $\mathrm{Th}^{\cdot+}$ and AnH (eq. 6 and 7), which, in the presence of sufficient $\mathrm{Th}^{\cdot+}$, could be oxidized in a second-order kinetic pathway (eq. 8 and 9).

$$Th^{\cdot +} + AnH \rightleftharpoons (Th/AnH)^{\cdot +} \qquad (6)$$

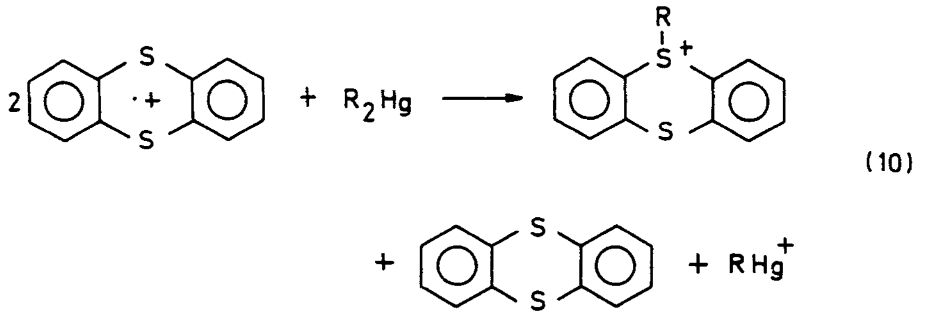
$$(Th/AnH)^{\cdot +} \rightleftharpoons Th + AnH^{\cdot +} \qquad (7)$$

$$(Th/AnH)^{\cdot +} + Th^{\cdot +} \rightleftharpoons (Th/AnH)^{2+} + Th \qquad (8)$$

$$(Th/AnH)^{2+} \longrightarrow (ThAn)^{+} + H^{+} \qquad (9)$$

Equations 6 and 7 show, of course, a net electron transfer reaction. The fate of escaped $AnH^{\cdot +}$ in this case was not followed, but in analogous (but slightly dif,ferrent in overall detail) reactions with dibenzodioxin cation radical, the $AnH^{\cdot +}$ ended finally as 4,4'-dimethoxybiphenyl and its cation radical [6]. We see here the beginning of electron-transfer-initiated chemistry of organosulfur cation radicals.

The probable occurrence of electron transfer in other organosulfur cation-radical reactions became evident in studies of reactions of organomercurials with $Th^{\cdot +}$ and phenoxathiin cation radical. It had been found that a number of diaryl mercurials and dimethyl mercury reacted cleanly with $Th^{\cdot +}$ to cause arylation (and methylation) on sulfur (eq. 1o). These reactions were initially



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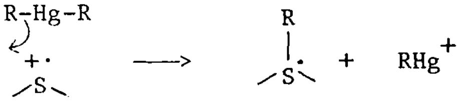
looked upon as involving electrophilic displacement of R from $R_2Hg$ by $Th^{\cdot +}$ (shown schematically in eq. 11 and 12). However, reaction with diethyl mercury gave far more thianthrene (Th) than allowable by the stoichiometry of eq. 10. It appeared that electron transfer could be occurring and that the pathway to the sulfonium-ion product (designated as $ThR^+$) should, in fact, be initiated also by electron transfer (eqs. 13-15)[7]. These equations show an initial electron transfer (eq.13) followed by the decomposition of $R_2Hg^{\cdot +}$, a reaction



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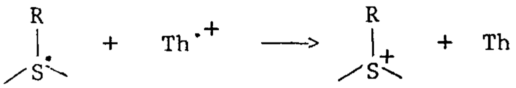


(12)

$$Th^{\cdot +} + R_2Hg \rightleftharpoons Th + R_2Hg^{\cdot +} \qquad (13)$$

$$R_2Hg^{\cdot +} \longrightarrow R^{\cdot} + RHg^{+} \qquad (14)$$

$$Th^{\cdot +} + R^{\cdot} \longrightarrow (ThR)^{+} \qquad (15)$$

$$(Th/R_2Hg)^{\cdot +} \longrightarrow Th + R^{\cdot} + RHg^{+} \qquad (16)$$

$$(Th/R_2Hg)^{\cdot +} + Th^{\cdot +} \longrightarrow (ThR)^{+} + RHg^{+} + Th \qquad (17)$$

which had been shown earlier by Kochi, in reaction of dialkyl mercurials with hexachloroiridate ion, to be very fast [8]. Decomposition of $R_2Hg^{\cdot +}$ gives radicals ($R^{\cdot}$), which are scavenged (eq. 15) only partly by $Th^{\cdot +}$ in forming the addition product $(ThR)^+$. Hence, an excess of Th results, which is attributable to the electron transfer reaction. Whether these details are correct, or whether perhaps another route to $(ThR)^+$ prevails, e.g. as in eqs. 16 and 17 is not known. What is known, though, is that ethyl radicals are indeed formed in the reactions with diethyl mercury. Sugiyama and Shine[1] showed that, when this reaction was carried out under oxygen, ethyl radicals were scavenged by $O_2$. Acetaldehyde, ethanol, and thianthrene 5-oxide (ThO) were formed. Further, when $^{18}O_2$ was used the oxygenated products contained $^{18}O$. Most interestingly, thianthrene 5,1o-dioxide ($ThO_2$) was also formed, a product which has never been obtained in other reactions of a nucleophile with $Th^{\cdot +}$. Sugiyama and Shine suggested the following possibilities (eqs. 18-21) as viable reactions, but again no attempts have been made to verify them in other ways.

$$Et^{\cdot} + O_2 \longrightarrow EtO_2^{\cdot} \qquad (18)$$

$$EtO_2^{\cdot} \longrightarrow CH_3CHO/CH_3CH_2OH \qquad (19)$$

$$Th + EtO_2^{\cdot} \longrightarrow ThO + EtO^{\cdot} \qquad (2o)$$

$$ThO + EtO_2^{\cdot} \longrightarrow ThO_2 + EtO^{\cdot} \qquad (21)$$

## CURRENT WORK

To our knowledge the work by Sugiyama and Shine was the first to show that $Th^{\cdot +}$ could induce alkyl radical reactions by an initial electron transfer step [1]. This and the intriguing possibility that $Th^{\cdot +}$ might be an efficient scavenger for radicals (eq. 15) led to the work which is in progress and some of which is now described.

## Reactions of $Th^{\cdot +}$ with Azoalkanes.

Our initial objective was to generate alkyl radicals at room temperature in the presence of $Th^{\cdot +}$ by the well known photolysis of azoalkanes. The plan seemed to be a promising one because there is a "window" in the uv-visible spectrum of $Th^{\cdot +}$ which would allow for irradiation of an azoalkane. However, it was soon found that the azoalkanes which were chosen underwent rapid reaction with $Th^{\cdot +}$ in the absence of light, leading to the reduction of $Th^{\cdot +}$ and ensuing reactions of alkyl cations and radicals.

### Reaction with 1,1'-azoadamantane

1,1'-Azoadamantane undergoes thermal decomposition in solution at reasonable rates only at rather high temperatures (270°C)[9]. Irradiation of azoadamantane at ambient temperatures causes isomerization of the stable trans- into the more labile cis-isomer, and decomposition of the cis isomer into radicals occurs at reasonable rates only if the solution is warmed[10-12]. In contrast reaction of azoadamantane with $Th^{\cdot +}$ in acetonitrile at ambient temperature rapidly produced nitrogen and Th in quantitative yield. Only two other products could be found by isolation: N-adamantylacetamide, accounting for 90% of the adamantyl groups, and biadamantyl (biada), accounting for 3-4% of the adamantyl groups. A small amount of adamantanol (0.6%) and, surprisingly, only a very small amount (0.3%) of adamantane could be found by gc analysis. Careful, repeated measurement of the stoichiometry of the reaction showed that 1.77 mol of $Th^{\cdot +}$ was used per mol of

TABLE I Determination of Molar Ratio of Reactants in Reaction of Thianthrene Cation Radical Perchlorate with 1,1'-Azoadamantane in Acetonitrile. [a]

| Run | $Th^{\cdot +}$ $ClO_4^-$ mmol | Azo mmol | Time of stirring,h | Mole Ratio $Th^{\cdot +}$/azo |
|---|---|---|---|---|
| 1 | 0.8145 | 0.4654 | 4 | 1.77 |
| 2 | 0.9998 | 0.5661 | 40 | 1.77 |
| 3 | 1.0001 | 0.5688 | 40 | 1.76 |
| 4 | 2.0001 | 1.1299 | 15 | 1.77 |
| 5 | 1.0001 | 0.5653 | 3 | 1.77 |
| 6 | 2.0001 | 1.1292 | *b* | 1.77 |

*a*, Solid reactants were placed together in a septum-sealed reaction vessel under argon and 40 mL (30 mL in run 1) of dry solvent was injected by syringe. In runs 1-4 the initial ratio of weighed reactants was 2.00 : 1.00. After stirring (see time), more azo was added in small increments to discharge the color of $Th^{\cdot +}$. The data record the final complete amount of azo used. In runs 5 and 6 the amounts of reactants weighed initially had the mole ratio shown. In these cases the color of $Th^{\cdot +}$ was dispelled quickly. *b*, left vernight for convenience.

The simplest explanation of these findings is expressed in eqs. 22-25. The equations tell us that if oxidation

$$Th^{\cdot +} + AdN{=}NAd \longrightarrow Th + AdN{=}NAd^{\cdot +} \quad (22)$$

$$AdN{=}NAd^{\cdot +} \longrightarrow Ad\cdot + ad^{+} + N_2 \quad (23)$$

$$Ad\cdot + Th^{\cdot +} \longrightarrow Ad^{+} + Th \quad (24)$$

$$Ad^{+} + CH_3CN \longrightarrow \longrightarrow AdNHCOCH_3 \quad (25)$$

of adamantyl radicals by $Th^{\cdot+}$ were 100% efficient the ratio of reactants would be 2 $Th^{\cdot+}$: azoadamantane. The equations allow for a change in this ratio by $Ad^{\cdot}$ escaping oxidation and undergoing other reactions, such as dimerization and hydrogen abstraction. In that case, more azoadamantane would be needed for reaction with unused $Th^{\cdot+}$ and this would account for the ratio (1.77: 1) which we have measured. It is interesting to note that the generation of an alkyl radical and its subsequent oxidation to an alkyl cation has been proposed in reactions of tris-p-bromophenylamine cation radical with carboxylates by Schmidt and Steckhan (eqs. 26-28)[13].

$$Ar_3N^{\cdot+} + RCO_2^- \longrightarrow Ar_3N + RCO_2^{\cdot} \quad (26)$$

$$RCO_2^{\cdot} \longrightarrow R^{\cdot} + CO_2 \quad (27)$$

$$Ar_3N^{\cdot+} + R^{\cdot} \longrightarrow Ar_3N + R^+ \quad (28)$$

The same authors have made an analogous proposal in reactions of tris-p-bromophenylamine cation radical with alkyl p-anisyl ethers[14]. In our work with azoadamantane, however, this type of straightforward and attractive explanation may not be valid. We have been unable to find more than traces of adamantane by assiduous searches. We feel that if substantial amounts of free adamantyl radicals had been formed (eq. 23) hydrogen abstraction from solvent should have led to our finding larger amounts of adamantane.

Photochemical decomposition of azoadamantane in a number of hydrocarbon solvents has been reported earlier to lead, in fact, to large amounts of adamantane and biada[11]. We have carried out a similar decomposition in acetonitrile and have obtained similar results. It may be, then, that reaction of $Th^{\cdot+}$ with azoadamantane follows a course in which few adamantyl radicals are free, and that the adamantyl cation is formed before the azoadamantane cation radical decomposes. Two routes would allow for this possibility. One is that the cation radical is again oxidized (eqs. 29 and 3o) before much of it can decompose. The other is that complexation occurs (eq. 31), as proposed earlier for the anisole reaction by Parker [5], and that the second oxidation step occurs as shown in eq. 33. This would allow for a small amount of competing decomposition of the azoadamantane cation radical. At present, these suggestions are on uncertain grounds and are in need of clarification. It is not clear, for example, whether one can compare the fate of radicals produced in photochemical reactions with that in

$$\text{AdN=NAd}^{\cdot +} + \text{Th}^{\cdot +} \rightleftharpoons (\text{AdN=NAd})^{2+} + \text{Th} \qquad (29)$$

$$(\text{AdN=NAd})^{2+} \longrightarrow 2\ \text{Ad}^{+} + \text{N}_2 \qquad (3o)$$

$$\text{Th}^{\cdot +} + \text{AdN=NAd} \rightleftharpoons (\text{Th/AdN=NAd})^{\cdot +} \qquad (31)$$

$$(\text{Th/AdN=NAd})^{\cdot +} \rightleftharpoons \text{Th} + \text{AdN=NAd}^{\cdot +} \qquad (32)$$

$$(\text{Th/AdN=NAd})^{\cdot +} + \text{Th}^{\cdot +} \longrightarrow 2\ \text{Ad}^{+} + 2\text{Th} + \text{N}_2 \qquad (33)$$

electron transfer reactions. We do not know yet, that is, how well hydrogen abstraction from solvents by a radical can compete with electron-transfer oxidation of the radical. It is notable that in the reactions of Schmidt and Steckhan, the amounts of alkane and alkylacetonitrile which were obtained (presumed to be formed by radical reactions with acetonitrile solvent) were always small as compared with amounts of cation-based reaction products [13], leading us to sense that in those cases, too, oxidation of radicals prevailed.

It is possible that in our work adamantyl radicals are formed and add efficiently to the nitrile group of the solvent and the resulting adduct is oxidized to provide the way for N-adamantylacetamide (eqs. 34, 35). However, there are, to our knowledge, no precedents for such additions of radicals to acetonitrile.

$$\text{Ad}^{\bullet} + CH_3CN \rightleftharpoons \text{AdN}{=}\dot{C}{-}CH_3 \qquad (34)$$

$$\text{Th}^{\bullet +} + \text{AdN}{=}\dot{C}{-}CH_3 \longrightarrow \text{Th} + \text{AdN}{=}\overset{+}{C}{-}CH_3 \qquad (35)$$

The summary of the reaction of $\text{Th}^{\bullet +}$ with 1,1'-azoadamantane is that efficient oxidation of the azo compound occurs, predominantly at the two-electron level, resulting mainly in the trapping of the adamantyl cation by solvent[15]. A summary of the products is given in Table 2.

TABLE 2: Products of Reaction of Thianthrene Cation Radical Perchlorate with 1,1'-Azoadamantane in Acetonitrile [a]

| Product | % |
|---|---|
| Nitrogen | 101 |
| Thianthrene [b] | 101 |
| Thianthrene 5-oxide [d] | tr. |
| N-Adamantylacetamide [b,c] | 90 |
| 1,1'-Biadamantyl [b,e] | 3 |
| 1-Adamantanol [d] | 0.6 |
| Adamantane [d] | 0.3 |

a, Mole ratio was 1.77:1 except in nitrogen measurement, in which the ratio was 1.86:1.

b, By isolation

c, As the protonated perchlorate salt. Neutralization and gc determination of N-adamantylacetamide gave 81% yield.

d, By gc determination, 10% SE30 on Chromotorb W.

e, Precipitated during reaction.

We note finally in describing our work with azoadamantane an initially misleading observation which was made in its early stages. When searching for reaction products initially by gc, the reaction solution itself was injected into the column (protected by a guard column). Adamantane was observed in significant but variable amounts. It was found that this was being formed, either on the column (150°C) or in the injection port (250°C), by decomposition of $Ad\overset{+}{N}H_2COCH_3ClO_4^-$. Decomposition of the authentic salt was found to give adamantane, and another, unidentified, compound, when injected in the same way. Thereafter, gc analysis of products was carried out only after neutralization of the reaction solution with potassium hydroxide and extraction of the products.

Reaction with phenylazotriphenylmethane (PAT)

Thermal decomposition of PAT is well known as a source of phenyl radicals in solution, and has also played a large role in answering questions of one- or two-bond scissions in the decomposition of azo compounds [16,17]. Reaction (in suspension) with $Th^{\cdot+}$ in acetonitrile at ambient temperature took place readily with the evolution of nitrogen. Although extensive studies of the stoichiometry of reaction were not carried out, it appears that it has a molar ratio close to 2.o : 1.o. When reaction was complete, the visible spectrum of $Th^{\cdot+}$ (541 nm) was replaced with that of the triphenylmethyl cation (43o and 4o6 nm) plus a small band of unknown origin at 5oo nm [18]. These bands disappeared on addition of water to the solution. Reaction with PAT is similar to but more complex than with azoadamantane. More products were formed, many of them in amounts too small to be identified as yet. Thus, TLC of the reaction mixture showed

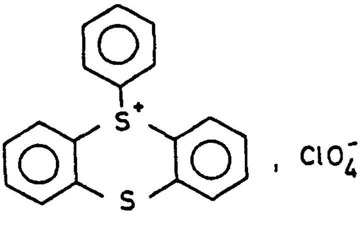
1o spots, while after work up, the mixture of products had 17 peaks in its HPLC chromatogram. Major products were identified and assayed by a combination of direct isolation (Th and the sulfonium perchlorate 1), quantitative analytical HPLC, and recycle preparative HPLC. The sulfonium salt (1) was identified by $^{1}H$ NMR and comparison with an authentic sample prepared by reaction of $Th^{\cdot +}$ with diphenyl mercury[7]. The major products are listed in Table 3.

TABLE 3 Major Products of Reaction of Thianthrene Cation Radical Perchlorate with Phenylazotriphenylmethane[a,b] in Acetonitrile

| Product | % |
|---|---|
| Nitrogen[c] | 92.2[d] |
| Thianthrene | 77.2[e] |
| Thianthrene 5-oxide | 3.2[e] |
| Sulfonium Salt (1) | 5o.1[d,f] |
| Triphenylmethanol | 73.7[d] |
| Acetanilide | 13.6[d] |
| Benzene | 6.5[d] |
| Carbinol (2) | 5.2[d] |

[a], From 1.oo mmol of $Th^{\cdot +}$ $ClO_4^-$ and o.5oo mmol of PAT in 3o mL of acetonitrile. [b], All products except $N_2$, 1 and 2 were assayed by analytical HPLC. [c], From a separate reaction of molar ratio 1.93 : 1.oo. [d], Based on PAT. [e], Based on $TH^{\cdot +}$. [f], 25.1% based on $Th^{\cdot +}$.

They account for 1o5% of the $Th^{\cdot +}$ used, 7o.2% of the phenyl groups and 73.7% of the triphenylmethyl groups in the PAT. Seven smaller products were isolated by preparative HPLC. Six of these were in amounts of 1-3 mg and remain unidentified. The seventh, (8,7 mg), appears from $^1H$ NMR and mass spectrum to have the structure 2, in which case it accounts for 5.2% of both phenyl and triphenylmethyl groups.



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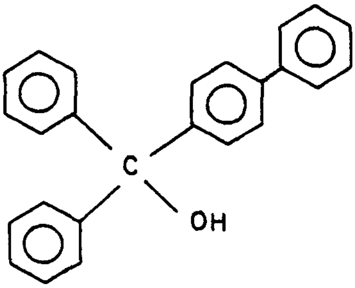


2

Formation of ThO (3.2%) suggests that 6.4% of $Th^{\cdot +}$ remained unreacted when water was added to the reaction mixture. Assay of the $N_2$ evolved was carried out in a separate reaction with a molar ratio of reactants of 1.93 : 1.oo but gave only 92% of the available $N_2$. Products that might have been formed but which could not be found by HPLC included biphenyl, triphenylmethane, Ntriphenylmethylacetamide, and the dimer of triphenylmethyl (so-called hexaphenylethane).

The products which we have identified give us significant information. Benzene (6.5%) and $\underline{1}$ (50.1%) suggest that phenyl radicals are trapped by solvent and $Th^{\cdot +}$ respectively. If this is correct, it would mean that $Th^{\cdot +}$ is a more efficient scavenger of phenyl radicals than solvent. However, the sulfonium ion may have been formed via reaction with a Parker-type complex (eq. 35),

$$(Th/PAT)^{\cdot +} + Th^{\cdot +} \longrightarrow \underline{1} + Th + Ph_3C^{+} \qquad (35)$$

rather than by the scavenging of free phenyl radicals. Certainly, the most likely source of benzene is the phenyl radical. The formation of acetanilide suggests that phenyl cations are formed and react with solvent, though we cannot rule out addition of phenyl radical to the nitrile group followed by oxidation of the resulting radical ($PhN{=}\dot{C}{-}CH_3$) by $Th^{\cdot +}$. Thus, the questions that pervade the work with PAT are whether phenyl radicals or phenyl cations are formed [19] and whether a complex (eq. 35) is involved. As for the triphenylmethyl portion of PAT, there is no doubt from spectroscopic evidence that the cation was formed, and that it did not add to acetonitrile at room temperature. Instead it remained (perhaps in equilibrium with the perchlorate) available for conversion into triphenylmethanol [21].

TABLE: Products [a] of Reaction of Thianthrene Cation Radical Perchlorate with Azotoluene in Acetonitrile [b]

| Product | % | mmol |
|---|---|---|
| Thianthrene | 88.3 [c] | 0.883 |
| Thianthrene 5-oxide | 12.0 [c] | 0.120 |
| Bibenzyl | 18.7 [d] | 0.105 |
| N-Benzylacetamide | 54.1 [d] | 0.606 |
| Triazole (4) | 25.6 [d] | 0.143 |

[a] Isolated by preparative TLC. Thianthrene and bibenzyl were not separable and were assayed in their mixture by $^1$H NMR.

[b] Molar ratio $Th^{\cdot+}$: azo was 1.79:1.00.

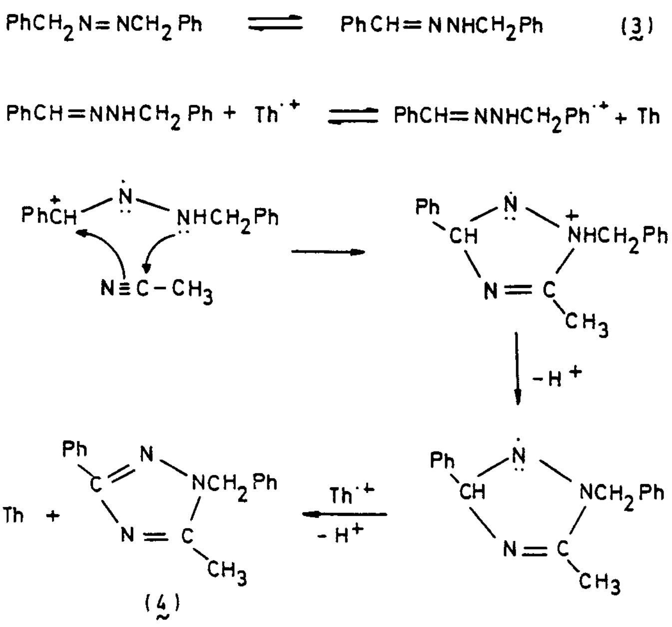
[c] Based on $Th^{\cdot+}$.

[d] Percentage of azotoluene used in forming product.

Reaction with Azotoluene

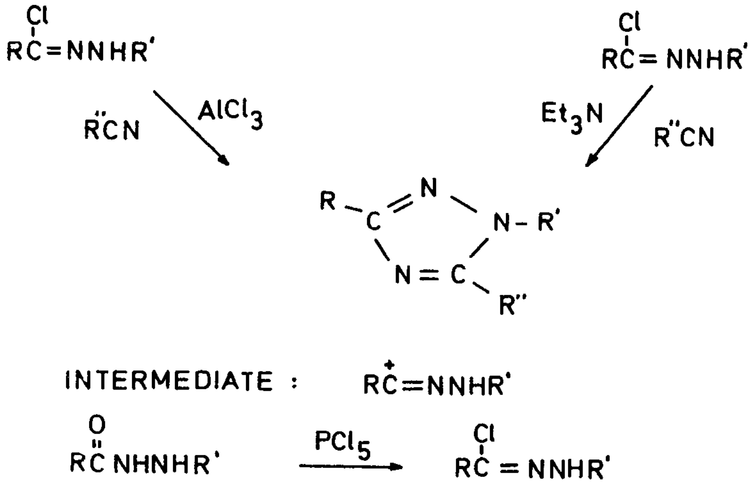
The products of this reaction are listed in Table 4. It is seen that substantial amounts of bibenzyl and N-benzylacetamide were formed, indicating that, in this case, both alkyl cation and radical were generated. Thus, here we can feel assured that the azoalkane cation radical does decompose (eq. 36). This occurrence may be rationalized by attributing the decomposition to the relative stability of the two benzylic fragments. Most interesting and extraordinary is the formation of the triazole (4) identified by $^1$H NMR and mass spectrometry. The source of the triazole is undoubtedly cycloaddition of solvent acetonitrile to an oxidized form of benzaldehyde benzylhydrazone (3) . This is represented in Scheme 1 where we use the cation radical of the hydrazone rather than the more oxidized form, the

Scheme 1



Scheme 2

METHODS OF PREPARING TRIAZOLES



deprotonated dication. Azotoluene is known to tautomerize easily and we represent the hydrazone as being formed in this way, but it may be that it is the cation radical of azotoluene which tautomerizes rather than azotoluene itself. In any event, this is an entirely new type of reaction whose scope we are now exploring. It is interesting to note that 1,2,4-triazoles are made customarily by cycloadditions, as shown in Scheme 2 [23,24]. The cation-radical initiated cycloaddition is identical in principle with the earlier syntheses, but the necessary two-electron oxidation stage of the hydrazone is reached in steps perhaps as we have shown in Scheme 1. Table 4 shows that a substantial amount of thianthrene 5-oxide (ThO) was formed. The source of ThO is the reaction of $Th^{\cdot +}$ with water. Since considerable care was taken to dry the solvent and exclude moisture during reaction, it is probable that $Th^{\cdot +}$ remained unused (and undetected in the colored reaction mixture) after addition of azotoluene was stopped. Reaction was carried out by slowly adding azotoluene in acetonitrile to the $Th^{\cdot +}$ solution until the color of the $Th^{\cdot +}$ appeared to have been dispersed. Thus, the ThO is believed to have been formed in working up the reaction mixture.

Table 4 shows that more N-benzylacetamide than bibenzyl is obtained. If these two products were formed solely from fragments as obtained in eq. 36 we would expect to find twice as many mmol of N-benzylacetamide as bibenzyl. The experimental result however was o.6o6 mmol of N-benzylacetamide and o.1o5 mmol of bibenzyl. Obviously,

$$PhCH_2N{=}NCH_2Ph^{\cdot +} \longrightarrow PhCH_2^{+} + PhCH_2^{\cdot} + N_2 \qquad (36)$$

$$2\ PhCH_2^{\cdot} \longrightarrow PhCH_2CH_2Ph \qquad (37)$$

$$PhCH_2^{+} + CH_3CN \longrightarrow \quad \longrightarrow PhCH_2HCOCH_3 \qquad (38)$$

then, more benzyl cations are formed than can be produced by eq. 36, and it seems therefore that again we must invoke either the oxidation of benzyl radicals (e.g., as in eq. 24) or the oxidation of a complex of $Th^{\cdot +}$ and azo compound, as in eq. 33.

## Reaction with azo-t-butane (ATB)

This reaction appears superficially to be quite clean and simple, but in reality has some complexity. Oxidation to the two-electron stage was complete, with a stoichiometry of 2.o $Th^{\cdot +}$:1.o ATB. Thus, t-butyl cations appear to be formed entirely (eq. 39). Consistent with this was the measurement of the nitrogen evolved. At a 1.o:1.o molar ratio 54% of the available $N_2$ was evolved, meaning that insufficient $Th^{\cdot +}$ was present to oxidize all of the ATB. At a 2.o:1.o molar ratio all of the $Th^{\cdot +}$ was converted into Th, and $N_2$ evolution was 1oo%. Curiously, however, although N-t-butylacetamide was formed (approx 8o% was isolated), the formation of its precursor cation (eq. 41) was not instantaneous. Also, although isobutene was obtained by injecting the reaction solution onto a gc column (BEEA/Chromosorb W) the isobutene was not present as truly free isobutene. That is, pumping off volatile products from the reaction mixture and trapping them in liquid nitrogen failed to give the large amounts of isobutene which appeared initially by gc to be present in the reaction mixture. Injection of aqueous bicarbonate solution into the reaction solution soon after reaction was complete gave not only N-t-butylacetamide but also substantial amounts of t-butanol, indicating that t-butyl cations were available in solution and had not yet reacted with solvent acetonitrile. The situation was analogous, in fact, to that in the case of PAT in which $Ph_3C^+$ cations remained available for conversion into triphenylcarbinol. It appears that t-butyl cations, formed as in eq. 39, were present in the reaction solution, perhaps in equilibrium with t-butyl perchlorate, and that their concentration decreased as they reacted slowly with solvent (eq. 4o,41). We are uncertain yet as to whether or not eq. 41 should be shown as reversible.

$$2\ Th^{\cdot +} + tBuN{=}NtBu \longrightarrow 2\ Th + 2\ tBu^+ + N_2 \tag{39}$$

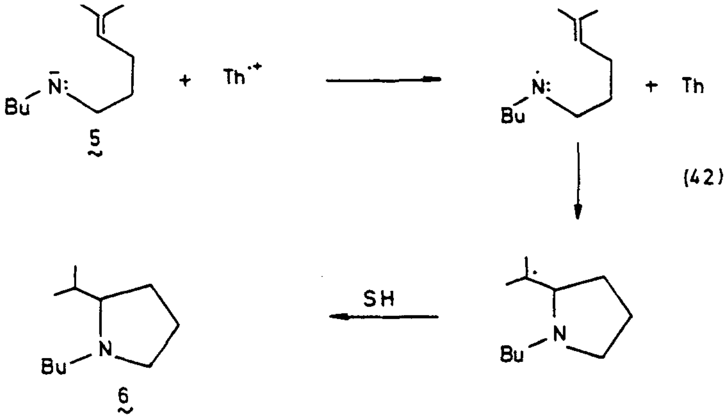
$$tBuClO_4 \rightleftharpoons tBu^+ + ClO_4^- \tag{4o}$$

$$tBu^+ + CH_3CN \longrightarrow CH_3\overset{+}{C}{=}NtBu \tag{41}$$

Although oxidation of all t-butyl groups in ATB appeared to be complete from the reaction stoichiometry and the quantitative yield of nitrogen, we were able also to find evidence for the formation of free t-butyl radicals. That is, reaction in the presence of $^{18}O_2$ led to the formation of $Th^{18}O$ and $Th^{18}O_2$, as shown by the relative abundances of the masses 232/234 and 248/252 in the mass spectra. Thus, scavenging of t-butyl radicals occurred and the t-butylperoxy radicals led to ThO and $ThO_2$, in the same way as experienced earlier with oxygen scavenging in the reactions with $Et_2Hg$ (see eqs. 18-21). It appears, then that oxygen was able to compete with $Th^{\cdot +}$ in scavenging t-butyl radicals.

## Reactions of $Th^{\cdot +}$ with Grignard Reagents

Very little is known about reactions of cation radicals of any kind, let alone organosulfur cation radicals, with strongly basic nucleophiles, such as $R^-$, $OR^-$, $NH_2^-$, $NR_2^-$. Eberson has commented on this gap in our knowledge of cation radical reactions [3g, 25]. Electron transfer has been shown, in collaborative work with Prof. M. Newcomb, to occur with the probe 5 which underwent SET and cyclization to 6 in reaction with $Th^{\cdot +}$ (eq. 42) [26]; and some indications of SET were obtained in my laboratory years ago in reactions of $Th^{\cdot +}$ with t-butoxide ion [26].



Recently we began studying reactions of $Th^{\cdot +}$ with Grignard reagents and these are the subject of the second part of this report.

In principle a Grignard reagent may react with $Th^{\cdot +}$ either by direct additions (eqs. 43 and 44) or by addition following electron transfer (eqs. 45, 46). These possibilities are, in fact, analogous to those in reactions of $Th^{\cdot +}$ with

$$Th^{\cdot +} + RMgX \longrightarrow ThR^{\cdot} + MgX^{+} \qquad (43)$$

$$ThR^{\cdot} + Th^{\cdot +} \longrightarrow ThR^{+} + Th \qquad (44)$$

$$Th^{\cdot +} + RMgX \longrightarrow Th + R^{\cdot} + MgX^{+} \qquad (45)$$

$$R^{\cdot} + Th^{\cdot +} \longrightarrow ThR^{+} \qquad (46)$$

$R_2Hg$ mentioned earlier. The Grignard reactions are more difficult to deal with however, because oxygen cannot be used as a trap for radicals, and the reactions cannot be carried out homogeneously. Although it is probable that homogenous reaction of RMgX with $Th^{\cdot +}$ in acetonitrile may be fast enough to avoid reaction with acetonitrile itself, we have chosen to work with solutions of RMgX in THF and ether in which $Th^{\cdot +}ClO_4^-$ is insoluble. Further, we began this work by using commercially available, standardized solutions of Grignard reagents in ether and THF, but found after time-consuming searches, that some of the unknown products of our reactions in ether were, in fact, impurities in the Grignard solutions. They remain still unknown, but we turned to making our own Grignards from carefully purified halides and ether. Reactions were carried out under argon at 0°C by adding the Grignard reagent by syringe via a septum to a stirred suspension of $Th^{\cdot +}ClO_4^-$. After one hour of stirring, the mixture was frozen in liquid nitrogen, the apparatus was evacuated and all volatile materials in the mixture, including solvent, were distilled at 0°C into a receiver cooled in liquid nitrogen. The solution of volatiles was removed for quantitative analysis by gc. Anhydrous ether was added to the solid reaction residue in the reassembled apparatus. Water was injected to decompose unreacted Grignard, and the alkane so formed was distilled, along with solvent and other volatiles if present, in the evacuated apparatus as described earlier for gc assay. The new solid residue was then worked to precipitate a thianthreniumyl perchlorate, if present, from methylene chloride with ether, and to separate Th and ThO by column chromatography. Finally, in a control experiment, the Grignard itself was decomposed by injecting water into an aliquot under the same circumstances, and the volatile products were assayed by gc.

Reaction with n-butylmagnesium chloride in ether.

Let us state the products obtained first. They were butane, butene, octane, butanol, the mixed ether ethyl 1-methylpentylpentyl [$(CH_3CH_2CH_2CH_2CH(CH_3)OCH_2CH_3$, designated ME], thianthrene, thianthrene oxide, and 5-butylthianthreniumyl perchlorate (7). Search was also made by gc for products that could arise from the solvent, namely, bis(1-methylpentyl)ether and ethyl vinyl ether but they could not be found. Yields of products are given in Table 5. The last entry in Table 5 shows that an aliquot of BuMgCl contained dissolved butane, butene and octane. The third entry lists the volatile products obtained by decomposing such an aliquot with water. The butane formed (2.165 mmol), when corrected for that already present (o.2o1 mmol) is in fair agreement with the measured molarity of the Grignard, that is, 1.96 M as compared with 2.o7 M by direct titration. The first entry shows that when equimolar amounts of $Th^{\cdot+}$ and BuMgCl were used, there was insufficient $Th^{\cdot+}$ to react with all of the Grignard. That is, BuMgCl (o.791 mmol) remained to react with water added in the second stage. Since equimolar amounts of reactants had been used, it becomes evident that some reactions between $Th^{\cdot+}$ and BuMgCl involve two moles of $Th^{\cdot+}$ and one of BuMgCl. It is evident also from the amounts of octane formed that butyl radicals must be involved, being formed in an SET step. The mixed ether (ME) also appears to be best attributed to radical formation and combination reactions (eq. 53). Butanol (Table 5) was found in the second stage distil-

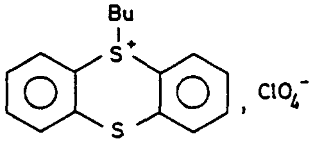


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TABLE 5. Products of Reaction of Thianthrene Cation Radical Perchlorate with Butyl Magnesium Chloride [a].

|  | Products (mmol) |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| Reactants | $C_4H_{10}$ | $C_4H_8$ | $C_8H_{18}$ | $C_4H_9OH$ | ME[b] | Th[c] | ThO[d] | ThBu$^+$[e] |
| $Th^{\cdot +}$/BuMgCl[f] | 0.571 | 0.016 | 0.120 | -- | 0.005 | 1.514 | 0.047 | 0.440 |
|  | 0.791 [h] |  |  | 0.167 [g] |  |  |  |  |
| $Th^{\cdot +}$/BuMgCl[i] | 0.826 | 0.016 | 0.230 | -- | 0.009 | 2.76 | 0.374 | 0.882 |
|  | 0.0 [h] |  |  | 0.039 [g] |  |  |  |  |
| BuMgCl/$H_2O$ [j] | 2.165 | 0.002 | 0.014 | -- | -- |  |  |  |
| BuMgCl [k] | 0.201 | 0.004 | 0.013 | -- | -- |  |  |  |

a, In ether at 0°C. In each case 1 ml of 2.07 M BuMgCl was used.
b, $CH_3(CH_2)_3CH(CH_3)OCH_2CH_3$. c, Thianthrene. d, Thianthrene 5-oxide.
e, 5-Butylthianthreniumyl perchlorate (7). f, Molar ratio 1.00:1.04.
g, Obtained in the second distillation after adding water.
h, $C_4H_{10}$ liberated in second stage, that is after removal of volatile products, redissolving dry residue in ether and injecting water. This represents BuMgCl which was unconsumed in reaction with $Th^{\cdot +}$.
i, Molar ratio 2.00 : 1.04. j, Addition of water to 1.0 ml of BuMgCl.
k, Volatile products in solution which contained 1.0 ml of BuMgCl, distilled off in vaccuo; no water added.

lation, after adding water to the residue of the first distillation. The source of the butanol is not known at the present time. Table 5 also lists ThO as a product. The reasonable source of this is hydrolysis of $Th^{\cdot +}$ by water occurring either adventitiously in starting out the reaction (first entry) or deliberately when an excess of $Th^{\cdot +}$ was used (third entry). To sum up, our basic premise is that electron transfer occurs (eq. 47) and that butyl radicals thus formed can dimerize, disproportionate, and be trapped by $Th^{\cdot +}$. In attempting to arrive at a material balance we are obliged to assume also that butane is formed by hydrogen abstraction from the solvent, and that the solvent radical suffers further loss of hydrogen to become ethyl vinyl ether (eq. 51,52). As mentioned above, we were unable to find this ether among the reaction products, but this is not surprising because we found, in separate experiments, that the authentic ether was readily polymerized by $Th^{\cdot +}$ in ether solution.

$$Th^{\cdot +} + BuMgCl \longrightarrow Th + Bu^{\cdot} + MgCl^{+} \qquad (47)$$

$$2\ Bu\cdot \longrightarrow C_4H_{10} + C_4H_8 \qquad (48)$$

$$2\ Bu\cdot \longrightarrow C_8H_{18} \qquad (49)$$

$$Th^{\cdot +} + Bu\cdot \longrightarrow ThBu^{+}\ (\underline{7}) \qquad (50)$$

$$Bu^{\cdot} + EtOEt \longrightarrow BuH + CH_3\dot{C}HOEt \qquad (51)$$

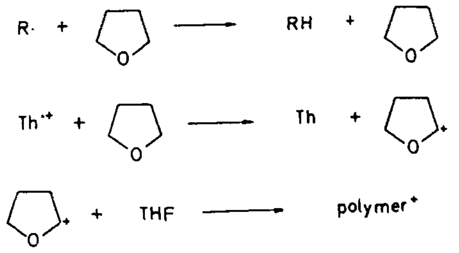
$$Bu^{\cdot} + CH_3\dot{C}HOEt \longrightarrow BuH + CH_2{=}CHOEt \qquad (52)$$

$$Bu^{\cdot} + CH_3\dot{C}HOEt \longrightarrow ME \qquad (53)$$

$$Th^{\cdot +} + CH_2{=}CHOEt \longrightarrow \text{polymer} \qquad (54)$$

## Reactions with Grignard Agents in THF

We have implicated dehydrogenation of solvent ether in the BuMgCl/ether reaction. Indications that the solvent was involved were quite firm in reactions in THF because each reaction led in varying extents to poly(THF). The reactions are not yet known with as much quantitative detail as in the BuMgCl/ether reaction but nevertheless have the following characteristics. Much of RMgX was converted into the alkane RH, and in some cases into small amounts of the dimer RR (R=Me, Et, iPr, nBu). Very little alkene was obtained. In all cases poly(THF) was formed and appeared to be the "living" polymer [27]. All indications pointed to cationic polymerization of THF. It appears that oxidation of the Grignard by $Th^{\cdot +}$ occurred (eq. 45) and that this led to abstraction of hydrogen atom from THF, followed by oxidation of the THF radical and polymerization (eqs. 55-57). Abstraction of $H^{\cdot}$ from THF has been shown by others to occur quite easily. In fact this occurs more easily than from cyclopentane (using $tBuO^{\cdot}$ [28]), from toluene (using $C_6H_5^{\cdot}$ [29]) and from ethylbenzene (using triplet anthraquinone [30]). We were unable to find the dimer of THF, a product which was found to a small extent in making 1-ethoxy-7-norbornylmagnesium bromide in THF [31] and in very high yield from heating t-butyl-peroxide in THF [32]. We were unable to find 1,2-dihydrofuran (DHF) either, but this is not surprising since, like ethyl vinyl ether, DHF was found not to survive in the presence of $Th^{\cdot +}$. The overall view of reactions in THF is then, that electron transfer occurs not only from RMgX but also from THF radicals. The curious apparent anomaly arises that cationic poly-



(55)

(56)

(57)

merization of THF was initiated in such basic systems, but "living" polymerization was sustainable only, of course, after all RMgX had been exhausted.

## SUMMARY

The thianthrene cation radical ($Th^{\cdot +}$), used as a model for organosulfur cation radicals, underwent electron-transfer reduction by a number of azoalkanes and Grignard reagents. This redox reaction induced, in turn, the oxidative decomposition of the reducing agents. Oxidation of the azoalkanes, moreover, reached the two-electron level to a large extent leading to both alkyl-radical and carbocation chemistry. Uncertainty exists, however, as to whether single electron transfer (SET) led to free alkyl radicals which were then oxidatively scavenged by a second $Th^{\cdot +}$, or whether, initially, complexation occurred between $Th^{\cdot +}$ and azoalkane, and was followed by both unimolecular and bimolecular (with a second $Th^{\cdot +}$) oxidative decomposition of the complex. In some cases the azoalkane was isomerized to the corresponding hydrazone, which underwent oxidative 1,3-dipolar cycloaddition to the solvent acetonitrile. The products of such reactions were 1,2,4-triazoles. In the case of Grignard reagents alkyl-radical chemistry was induced. The weight of evidence pointed to subsequent trapping of alkyl radicals by $Th^{\cdot +}$, giving a 5-alkylthianthreniumyl cation, and to hydrogen-atom abstraction from the solvent. Solvent involvement led ultimately to polymerization of the solvent; that is, as poly(THF) and (assumed) poly(vinyl ethyl ether). Reaction pathways are proposed speculatively in numbers of instances and have yet to be verified.

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