REACTION OF THIANTHRENE CATION RADICAL WITH DIARYLMERCURIALS. SEARCH FOR SINGLE ELECTRON TRANSFER IS ELUSIVE

A. K. M. M. HOQUE, Henry J. SHINE* and T. Krishnan VENKATACHALAM

Department of Chemistry and Biochemistry,
Texas Tech University, Lubbock, Texas 79409, U.S.A.

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Dedicated to Professor Václav Horák on the occasion of his 70th birthday.

Diarylmercurials (Ar_2Hg) with Ar = *p*-tolyl *Ib*, *o*-tolyl *Ic*, *p*-anisyl *Id* and 2-allyloxy-4,5-dimethylphenyl *Ie*, reacted with thianthrene cation radical perchlorate ($Th^{\bullet +}ClO_4^-$) in two stoichiometric ratios: 2 : 1 and 4 : 1 ($Th^{\bullet +}ClO_4^-/Ar_2Hg$). In the 2 : 1 ratio the products were the 5-arylthianthreniumyl perchlorates *IIb* – *IIe*, thianthrene (Th) and $ArHg^+ClO_4^-$ (assayed as ArHgCl, *III*) in quantitative yields. In the 4 : 1 ratio reaction with $ArHg^+$ occured, too, and the products were *IIb* – *IIe*, Th, the complex $Th_3Hg(ClO_4)_2$ and HgO (after workup). In contrast, Ph_2Hg (*Ia*) did not react beyond the 2 : 1 stoichiometry. In the reactions with *Ie*, no evidence for formation and cyclization of free 2-allyloxy-4,5-dimethylphenyl radical was found. Reaction of and product formation from these arylmercurials, therefore, does not occur in single electron transfer steps that lead to free aryl radicals. Instead electron transfer appears to occur within a complex of Ar_2Hg with $Th^{\bullet +}$ from which *II* and other products are subsequently formed.

Single-electron-transfer (SET) oxidations of alkylmetals in the lead, mercury and tin series have been studied extensively by Kochi and coworkers[1]. Substantial evidence for both inner and outer electron transfer in oxidations by, for example, $IrCl_6^{2-}$ and tris(phenanthroline)iron(III) complexes, leading to the formation of alkyl radicals, has been provided. In our own laboratory we have found evidence for SET in reactions of thianthrene cation radical perchlorate, $Th^{\bullet +}ClO_4^-$, with aryllithiums and aryl and alkyl Grignard reagents[2], with dialkylmercurials[3], and with tetraalkyl- and tetraryltins[4]. We were struck, in our earlier work, by the difference in reactions of, for example, PhMgCl and Ph_2Hg (ref.[2]). Evidence for the formation of phenyl radicals that was so marked in the former seemed to be absent in the latter. Reactions of diarylmercurials with $Th^{\bullet +}ClO_4^-$ had, in fact, been discovered in our laboratory almost 15 years earlier. At that time, too, the lack of signs of radical formation through SET was noted, although defi-

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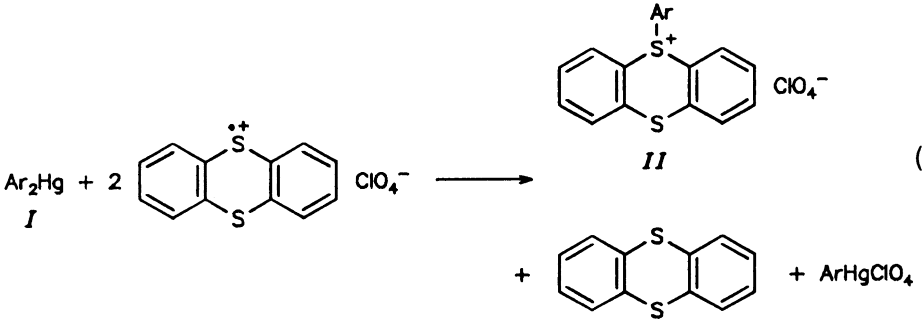
* The author to whom correspondence should be addressed.

nitive tests for radical formation were not then made. In order to clarify the apparent differences in patterns of reaction, we have now used a radical probe, di(2-allyloxy-4,5-dimethylphenyl)mercury (*Ie*), as a test of aryl radical formation in reaction with $Th^{\bullet +}ClO_4^-$. The basis of the test was that if the free 2-allyloxy-4,5-dimethylphenyl radical *VII* were formed from *Ie* after SET, it would cyclize and the cyclic radical *VIII* would show up in the products (vide infra). We have assumed that the rate of cyclization of *VII* would not be much different from that of the 2-allyloxyphenyl radical, namely $6.3 \cdot 10^9$ s^{-1} (ref.[5]) and, hence faster than the probable bimolecular rate of being trapped by $Th^{\bullet +}$. On the other hand, if cyclization was not observed, the 2-allyloxy-4,5-dimethylphenyl group would itself be found in the products, and indicate that *VII* had not been formed. We can report now that the latter is the case.

In all of our earlier work with diarylmercurials, reactions were carried out only in accord with the stoichiometry shown in Eq. (*1*). Once this stoichiometry had been established with Ph_2Hg (*Ia*) no further thought had been given to the possibility that the stoichiometry could be different, and all subsequent reactions with Ar_2Hg were carried out with quantities of reactants prescribed by the so-called 2 : 1 ($Th^{\bullet +}/Ar_2Hg$) ratio.



(*1*)

During our more recent work with dialkylmercurials we found, however, that di-tert-butylmercury and dibenzylmercury could react with $Th^{\bullet +}ClO_4^-$ not only with the customary 2 : 1 stoichiometry but also could undergo more extensive oxidation with a reactant ratio of 4 : 1 ($Th^{\bullet +}/R_2Hg$) (ref.[3]). The reason for this was that the tert-butylmercury cation and benzylmercury cation moiety was oxidized by an excess of $Th^{\bullet +}$ to the corresponding alkyl cation and Hg^{2+}. The Hg^{2+} then formed a complex *IV* with thianthrene (Eqs (*2*) and (*3*)).

$$R_2Hg + 4\,Th^{\bullet +}ClO_4^- \longrightarrow 4\,Th + 2\,R^+ + Hg^{2+} + 4\,ClO_4^- \qquad (2)$$

$$3\,\mathrm{Th} + \mathrm{Hg}^{2+} + 2\,\mathrm{ClO}_4^- \longrightarrow \mathrm{Th}_3\mathrm{Hg}(\mathrm{ClO}_4^-)_2 \quad (IV) \qquad (3)$$

In our work with *Ie* we found that it, too, could react in the 2 : 1 and 4 : 1 stoichiometric ratios, and because of that we re-examined some of reactions that had been reported earlier, namely, of *Ia*, di(*p*-tolyl)- (*Ib*), di(*o*-tolyl)- (*Ic*) and di(*p*-anisyl)mercury (*Id*). We report on those reactions, now, too.

EXPERIMENTAL

Diarylmercurials

Diphenyl- (*Ia*) and di(*p*-tolyl)mercury (*Ib*) were from commercial sources. Di(*o*-tolyl)- (*Ic*) and di(*p*-anisyl)mercury (*Id*) were prepared in the standard way from the reaction of the corresponding Grignard reagent and $HgBr_2$. Each was crystallized from absolute ethanol; *Ic* had m.p. 95 – 96 °C while *Id* had m.p. 198 °C.

Di(2-allyloxy-4,5-dimethylphenyl)mercury (*Ie*) was prepared in the following way. 2-Bromo-4,5-dimethylphenol (*V*) was prepared by brominating 3,4-dimethylphenol in acetic acid at 0 – 5 °C. After crystallization from petroleum ether the product had m.p. 78 °C and satisfactory ^{1}H NMR and mass spectra. Allyl (2-bromo-4,5-dimethyl)phenyl ether (*VI*) was prepared by reaction of *V* with allyl bromide in boiling acetone containing a suspension of K_2CO_3. The product was distilled under reduced pressure and had b.p. 120 °C/0.3 kPa and a satisfactory ^{1}H NMR spectrum. Compound *VI* was converted into its Grignard reagent in tetrahydrofuran (THF) solution under activation with 1,2-dibromoethane. The Grignard reagent was converted into *Ie* by reaction with $HgBr_2$ in THF in the usual way. After crystallization from absolute ethanol *Ie* had m.p. 126 – 127 °C. For $C_{22}H_{26}HgO_2$ (523.0) calculated: 50.5% C, 4.98% H; found: 49.7% C, 4.94% H.

Arylmercury Chlorides

Phenylmercury chloride (*IIIa*) and *p*-tolylmercury chloride (*IIIb*) were from commercial sources; *o*-tolylmercury chloride (*IIIc*) and *p*-anisylmercury chloride (*IIId*) were isolated with TLC from the reactions of the corresponding Ar_2Hg with $Th^{\bullet+}ClO_4^-$, and had m.p. 138 – 140 °C and m.p. 230 – 231 °C, respectively, and satisfactory ^{1}H NMR spectra. 2-Allyloxy-4,5-dimethylphenylmercury chloride (*IIIe*) was prepared by reaction of *Ie* with $HgCl_2$ and had m.p. 155 – 157 °C and satisfactory ^{1}H NMR spectrum.

Preparation of 3,5,6-Trimethyl-2,3-dihydrobenzofuran (*IX*)

A solution containing 2.0 g of *VI*, 25 mg of azobis(isobutyronitrile) and 8 ml of Bu_3SnH in 30 ml of THF was boiled under reflux for 36 h. Workup and vacuum fractional distillation gave 800 mg of an oil, 85 – 90 °C/0.3 kPa with satisfactory ^{1}H NMR spectrum but containing a small amount of Bu_3SnBr, as indicated by the ^{1}H NMR spectrum. The product was chromatographed on a column of silica, but without removing the impurity completely.

Reaction of $Th^{\bullet+}ClO_4^-$ with Di(*p*-tolyl)mercury (*Ib*)

2 : 1 Ratio: To the solids $Th^{\bullet+}ClO_4^-$ (315 mg, 1.0 mmol) and *Ib* (191 mg, 0.50 mmol) placed side by side under argon in a 100 ml septum-capped flask was added 25 ml of MeCN by syringe. The mixture was stirred overnight by which time the color of $Th^{\bullet+}$ had disappeared. Aqueous 3 M LiCl solution (3 ml) was added and was followed by 2 ml of water. The mixture was extracted with 4 x 15 ml of CH_2Cl_2. The dried ($MgSO_4$) dichloromethane solution was evaporated to dryness in a rotary evaporator. The white residue that was obtained was dissolved in 10 ml of CH_2Cl_2. After addition of 30 ml of dry ether the cloudy solution was placed in the refrigerator overnight to give 193 mg (0.474 mmol) of *IIb*, having m.p. 199 – 200 °C after reprecipitation from CH_2Cl_2 with ether. The *IIb* had a satisfactory ^1H NMR spectrum. Evaporation of the filtrate gave 271 mg of white solid. This was dissolved in 10.0 ml of CH_2Cl_2 for GC assay of the Th and *IIIb* that were present. The results are listed in Table I, run 3.

4 : 1 Ratio: A solution of 473 mg (1.50 mmol) of $Th^{\bullet+}ClO_4^-$ in 20 ml of MeCN was added dropwise over a period of 1 h to a stirred solution of 143 mg (0.375 mmol) of *Ib* in 10 ml of MeCN. The color of $Th^{\bullet+}$ was dispersed after addition of 0.675 mmol of $Th^{\bullet+}$, whereupon a yellow precipitate began to form. Addition was continued until all of the $Th^{\bullet+}ClO_4^-$ had been added. At that time the color of the mixture was light purple. After overnight stirring the color of $Th^{\bullet+}$ had disappeared and a copious yellow precipitate had formed. The precipitate was removed by filtration and amounted to 164 mg (0.157 mmol) of *IV*, m.p. 279 – 280 °C (ref.[3]). To the filtrate was added 5 ml of water, and this was followed by extraction with 3 x 15 ml of CH_2Cl_2. The aqueous layer was saved for later assays, while the dried ($MgSO_4$) dichloromethane solution was evaporated to dryness and the residue was dissolved in 10 ml of CH_2Cl_2. Addition of 30 ml of ether gave 284 mg of *IIb* m.p. 199 – 200 °C, while GC assay of the filtrate gave 302 mmol of Th and 0.017 mmol of ThO. To the aqueous layer were added several drops of concentrated HCl. A white precipitate of Hg_2Cl_2 (8.4 mg, 0.018 mmol) was removed. The acidic filtrate was made alkaline with NaOH and a yellow precipitate of HgO (40.6 mg, 0.188 mmol) was obtained. The Hg_2Cl_2 was washed with HCl and the HgO with acetone before drying and weighing. The results are listed in Table I, run 4.

TABLE I

Products of reaction of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) with diarylmercurials (Ar_2Hg)

Run	Ar_2Hg	Ratio of reactants[a]	Products, mmol							Summations, %[b]		
			Th	ThO	*II*	*III*	*IV*	Hg_2Cl_2	HgO	Ar	Th	Hg
1	*Ia*	2 : 1	0.472		0.452	0.461				91.3	92.4	92.2
2	*Ia*	4 : 1	0.508	0.241	0.228	0.229				91.2	97.7	91.6
3	*Ib*	2 : 1	0.488		0.474	0.480				95.4	96.2	96.0
4	*Ib*	4 : 1	0.302	0.017	0.698		0.157	0.018	0.188	93.1	99.2	102
5	*Ic*	2 : 1	0.480		0.459	0.470				92.9	93.9	94.0
6	*Ic*	4 : 1	0.162		0.456		0.120	0.015	0.097	91.2	97.8	98.8
7	*Id*	2 : 1	0.481		0.463	0.470				93.6	94.4	94.0
8	*Id*	4 : 1	0.166		0.466		0.123	0.012	0.101	93.2	100	99.2
9	*Ie*	2 : 1	0.498		0.466	0.472				93.8	96.4	94.4
10	*Ie*	4 : 1	0.237		0.711		0.177	0.017	0.160	94.8	98.6	98.9

[a] In the 2 : 1 runs 1.0 mmol of $Th^{\bullet+}ClO_4^-$ and 0.50 mmol of Ar_2Hg were used; in the 4 : 1 runs the amounts were 1.50 and 0.375 mmol in runs 4 and 10, but 1.0 and 0.25 mmol in runs 2, 6, and 8. [b] The amount of each group found in the products.

Reaction of $Th^{\bullet+}ClO_4^-$ with Di(*o*-tolyl)mercury (*Ic*), Di(*p*-anisyl)mercury (*Id*) and Di(2-allyloxy-4,5-dimethylphenyl)mercury (*Ie*)

These reactions were carried out as with *Ib*. In the 2 : 1 reactions with *Id* and *Ie* the color of $Th^{\bullet+}$ disappeared within few minutes of stirring. Workup of these reactions followed as described for *Ib*. Results are listed in runs 5 – 10. Product *IIc* had m.p. 191 – 192 °C, *IId* had m.p. 160 – 161 °C, and *IIe* had m.p. 111 – 112 °C, each after reprecipitation and each had a satisfactory ^1H NMR spectrum[6].

Reaction of $Th^{\bullet+}ClO_4^-$ with Ph_2Hg (*Ia*)

2 : 1 Ratio: To a solution of 315 mg (1.0 mmol) of $Th^{\bullet+}ClO_4^-$ in 15 ml of MeCN was added a solution of 177 mg (0.50 mmol) of *Ia* in 10 ml of MeCN over a period of 2 h. Stirring was continued and the color of $Th^{\bullet+}$ disappeared after another 1 h. Three ml of 3 M LiCl was added, followed by 2 ml H_2O. Extraction with CH_2Cl_2 and workup followed in the usual way. The results are listed in run 1. The product *IIa* had m.p. 251 – 253 °C after reprecipitation from CH_2Cl_2 with ether.

4 : 1 Ratio: $Th^{\bullet+}ClO_4^-$ (315 mg, 1.0 mmol) and *Ia* (88.5 mg, 0.25 mmol) were used as above. Stirring was continued for 48 h after which the color of $Th^{\bullet+}$ persisted. Addition of 0.5 ml of H_2O caused the color of $Th^{\bullet+}$ to disperse but formation of the yellow solid *IV* was not observed. Workup with LiCl and H_2O followed in the usual way. The results are listed in run 2.

RESULTS AND DISCUSSION

Stoichiometry of Reaction

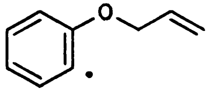
Each of the diarylmercurials (*Ia* – *Ie*) reacted cleanly with $Th^{\bullet+}ClO_4^-$ according to Eq. (*1*). 5-Arylthianthreniumyl perchlorates (*IIa* – *IIe*) were isolated in high yield and were characterized by ^1H NMR spectroscopy[6]. Thianthrene (Th) and $ArHg^+$ were obtained also in high yield, the latter being converted in workup to, and assayed with GC as, ArHgCl. The results are listed in Table I, runs 1, 3, 5, 7, and 9. Each of the diarylmercurials except *Ia* also underwent complete substitution reaction with $Th^{\bullet+}ClO_4^-$ at the 4 : 1 stoichiometric ratio. In that way, the aryl group was found solely, and in high yield, as the sulfonium salt *II*; none of ArHgCl *III* was obtained (Table I, runs 4, 6, 8, and 10). In the 4 : 1 reactions Hg in Ar_2Hg was obtained almost entirely as Hg^{2+}, both in the form of complex *IV* and as HgO. Small amounts (9 – 12%) of Hg_2Cl_2 were obtained, indicating that complete oxidation of Hg to the Hg^{2+} stage (Eq. (*2*)) had not occurred.

Diphenylmercury (*Ia*) was resistant to the total reaction. At the 4 : 1 ratio of reactants (run 2), $Th^{\bullet+}$ did not disappear completely even after 48 h of contact. The unused $Th^{\bullet+}$ was converted into Th and its 5-oxide (ThO) by the addition of water. The amount of ThO obtained (0.241 mmol) showed that 48% of the original $Th^{\bullet+}$ remained unused, as required by the stoichiometry of Eq. (*1*). The amounts of Th and PhHgCl that were obtained are also consistent with reaction according to Eq. (*1*) along with hydrolysis of unused $Th^{\bullet+}$ by water added later.

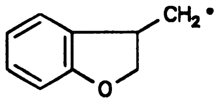
These results show that when the phenyl group contained an electron-donating substituent, even a moderate donor such as CH_3, an oxidative substitution reaction of $ArHg^+$ was possible.

The Reaction of Ie and the Mechanism of Reaction of Ar_2Hg *with* $Th^{\bullet+}ClO_4^-$

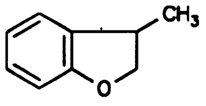
The product of reaction of *Ie* with $Th^{\bullet+}ClO_4^-$ is *IIe*. No indications of the formation of the radical *VII* and its cyclization to *VIII* were obtained. We found neither allyl 3,4-dimethylphenyl ether or cyclic product *IX*, that would have been formed by hydrogen atom abstraction from the solvent, nor the thianthreniumyl perchlorate (i.e., *IIf*, Ar = *VIII*) that would have resulted from trapping of the radical *VIII* by $Th^{\bullet+}$. If radical *VII* had been formed, therefore, it had to have been trapped so rapidly by $Th^{\bullet+}$ as to exclude the possibilities of reaction with solvent and of cyclization. Similarly, if reactions of *Ia* – *Id* involved the formation of free aryl radicals, their trapping by $Th^{\bullet+}$ would have to have been exclusive. We feel that this is not a reasonable hypothesis. Instead, it is more likely that the reactions of these diarylmercurials (*Ia* – *Ie*) with $Th^{\bullet+}$ occur within complexes such as have been proposed by Parker for reactions of $Th^{\bullet+}$ with anisole and phenol[7]. That is, in the 2 : 1 stoichiometry, reaction can be represented with Eqs (*4*) – (*6*). The product *II* is not formed by the trapping of aryl radical by $Th^{\bullet+}$ but by the collapse of the dicationic complex $(Ar_2Hg/Th)^{2+}$, Eq. (*6*). Because reactions of *Ib* – *Ie* can continue to the 4 : 1 stoichiometric level, the cation $ArHg^+$, or its perchlorate, $ArHgClO_4$, must also be capable of undergoing an oxidative substitution reaction with $Th^{\bullet+}$ without formation of free aryl radical. We represent this requirement with the formation of a radical dication complex (Eq. (*7*)) and its subsequent fate in Eqs (*8*) and (*9*) or Eq. (*10*).



VII



VIII



IX

The reactions that lead to products *II*, therefore, are overall electrophilic substitutions by cationic sulfur of the thianthrenium group at the *ipso*, Hg-bearing carbon atom of the benzene ring, *ortho* and/or *para* to the electron donating group. We chose to work with *Ie* rather than the simpler di(*o*-allyloxyphenyl)mercury because reactions with that, although occurring without formation and cyclization of the *o*-allyloxyphenyl radical, were more complex and led to substitution by the thianthrenium group not only at the

$$\mathrm{Ar_2Hg + Th^{\bullet +} \rightleftharpoons (Ar_2Hg/Th)^{\bullet +}} \tag{4}$$

$$\mathrm{(Ar_2Hg/Th)^{\bullet +} + Th^{\bullet +} \longrightarrow (Ar_2Hg/Th)^{2+} + Th} \tag{5}$$

$$\mathrm{(Ar_2Hg/Th)^{2+} \longrightarrow \mathit{II} + ArHg^{+}} \tag{6}$$

$$\mathrm{ArHg^{+} + Th^{\bullet +} \rightleftharpoons (ArHg/Th)^{\bullet 2+}} \tag{7}$$

$$\mathrm{(ArHg/Th)^{\bullet 2+} \longrightarrow \mathit{II} + Hg^{+}} \tag{8}$$

$$\mathrm{Hg^{+} + Th^{\bullet +} \longrightarrow Hg^{2+} + Th} \tag{9}$$

$$\mathrm{(ArHg/Th)^{\bullet 2+} + Th^{\bullet +} \longrightarrow \mathit{II} + Hg^{2+} + Th} \tag{10}$$

ipso, Hg-bearing carbon but also at the position *para* to the allyloxy group. The same type reaction occurred with di(*o*-anisyl)mercury. These reactions are being studied further.

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