Articles

Reactions of Two Isomeric Thiols with Thianthrene Cation Radical

Hyun-ju Park and Wang Keun Lee[*]
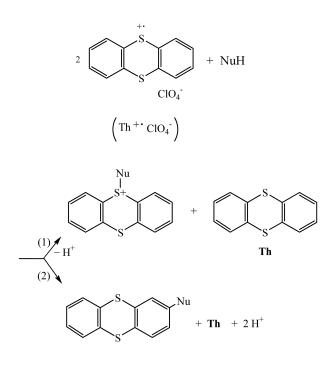
Chemistry Education Major, Faculty of Science Education, Chonnam National University, Gwangju 500-757, Korea
[*]*E-mail: wklee@chonnam.ac.kr*
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Thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) reacted readily with two isomeric thiols, benzylthiol (**1**) and 4-methylbenzenethiol (**7**) in an acetonitrile solution at room temperature. From the reaction of **1**, the major products, *N*-benzylacetamide (**4**) and benzyl sulfide (**5**), are characteristic of benzyl carbocations while the minor one, benzyl disulfide (**6**) implies free radical component of the reaction. It is unprecedented that the formation of a benzyl carbocation was caused by the extrusion of sulfur atoms from benzyl sulfur cations (**3**). In contrast, from the reaction of **7**, only *p*-tolyl disulfide (**10**) was obtained from both sulfur radicals and cations. In the reaction of **7** the thio-extrusion was not observed from the *p*-tolyl sulfur cation (**9**). A thianthrene cation radical ($Th^{+\cdot}$) was reduced quantitatively to thianthrene (Th) in both reactions.
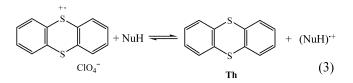
Key Words : Thianthrene cation radical, Thiols, Disulfide, Sulfide, Thio-extrusion

Introduction

The chemistry of thianthrene ($Th^{+\cdot}$) and other organo-sulfur cation radicals widened in scope not only because reactions with nucleophiles often led to the addition at sulfur and an occasional substitution in the rings (eq 1-2), but

cation radicals also underwent a one-electron transfer reaction represented with eq 3. For example, reactions of cation radicals with aliphatic and aromatic alcohols were explained via the addition mechanism.[1-5] But reactions of
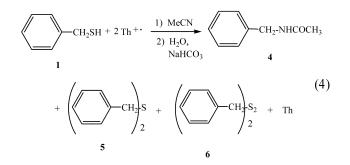

$$Th^{+\cdot} \text{ with organometals,}^{6-8} \text{ along with azoalkanes}^{9-11} \text{ and}$$

$Th^{+\cdot}$ with organometals,[6-8] along with azoalkanes[9-11] and carbonates,[12,13] occurred by an electron transfer mechanism. One of the most intensely, mechanistic studied reactions of $Th^{+\cdot}$ is with alcohols. Thiol is similar to alcohol and phenol, but it is surprising, then, that no analogous study of $Th^{+\cdot}$ reactions with thiols have been reported. This paper aims to discern whether the chemistry of $Th^{+\cdot}$ with thiols, leads to the addition at sulfur in the rings or undergoes a one-electron transfer reaction.

We have now carried out a systematic investigation of $Th^{+\cdot}$ reactions with two isomeric thiols, benzylthiol (**1**) and 4-methylbenzenethiol (**7**), in an acetonitrile solution at room temperature. Contrary to our expectations, the reactions were not analogous to those of the alcohol. The results can be understood on the basis that thiol cation radicals are formed by a one-electron transfer to $Th^{+\cdot}$ and lead to deprotonation, dimerization, second electron transfer, and substitution reactions of the S_N2 types. Two isomers of C_7H_8S lead to different reaction mechanisms depending on the stability of carbocations. This is an unusual reaction of thiols and offers the first example of cation radical induced oxidation.

Results and Discussion

Benzylthiol (1). A thermally stable **1** is readily oxidized by $Th^{+\cdot}$ in an acetonitrile solution at room temperature.

Products of the reaction were *N*-benzylacetamide, benzyl sulfide and benzyl disulfide. The products of these reactions are shown in equation 4. Quantitative results from GC
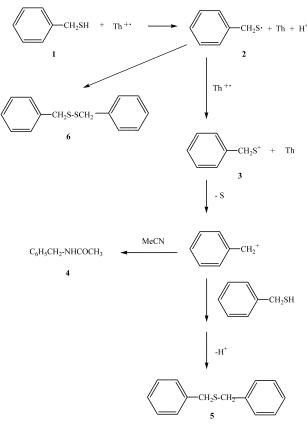

$$\tag{4}$$

measurements are given in Table 1. Product balances account for 102% of the benzyl groups which appears as 70% of benzyl carbocations, and 100% of the cation radicals.

In the present study, **1** was oxidized by Th$^{+\cdot}$ *via* an electron

Table 1. Products[a] of Reaction of Th$^{+\cdot}$ClO$_4^-$ with Benzylthiol (**1**) and 4-Methylbenzenethiol (**7**)

Thiol[b]	Th$^{+\cdot}$ClO$_4^-$	Acetamide	Disulfide	Sulfide	Th
1	100	62	24	16	100
7	100	–	88	–	98

[a]Th$^{+\cdot}$ClO$_4^-$ and products in mmol $\times$ 10^2. [b]Used in 0.5 mmol $\times$ 10^2, 50 mmol. Number of runs averaged were for **1** (five runs) and **7** (four runs).

Scheme 1

transfer.

This runs contrary to the reactions of phenol, where results are explicable in the formation of an 5-arylthianthreniumyl ion (HOArTh$^+$, Ar = phenol). The mechanism can be understood on the basis as shown in Scheme 1.

It is evident from the relatively high oxidation potentials (> 2 V) of alcohols[14] compared to Th (approx. 1.3 V *vs* SCE[15]), that the reaction of Th$^{+\cdot}$ with alcohols cannot originate in an oxidation reaction. But the redox potentials of thiols are normally in the same range or higher (0.7-1.1 V).[16,17] Therefore, the reaction of thiol with Th$^{+\cdot}$ can be explained with an electron transfer and the formation of a very labile thiol cation radical.

The thiol cation radical, **1**$^{+\cdot}$ is formed by one-electron oxidation of **1** and leads to a benzyl sulfur radical, **2** after the loss of a proton. The sulfur radical, **2** exhibited two subsequent transformations. An unprecedented and major pathway is the second oxidation of **2** with another Th$^{+\cdot}$ to yield the intermediate benzyl sulfur cation **3**. In the light of our results, the life time of **2** is long enough to be oxidized by Th$^{+\cdot}$ to **3**. The sulfur cation intermediate (**3**) readily loses sulfur atom to yield a benzyl carbocation. The most of benzyl carbocations react with the acetonitrile solvent to give *N*-benzylacetamide (**4**), Ritter type product. The rest of the benzyl carbocations were attacked by **1**, and benzyl-sulfide (**5**) were formed by S$_N$2 displacement.

The propensity to readily lose sulfur upon exposure to light or heat,[18] by cation radical,[19] through a treatment with a *tert*-phosphine under basic conditions[20,21] have been reported. To the best of our knowledge, this is the first example of thio-extrusion from a sulfur cation **3** to a benzyl carbocation.
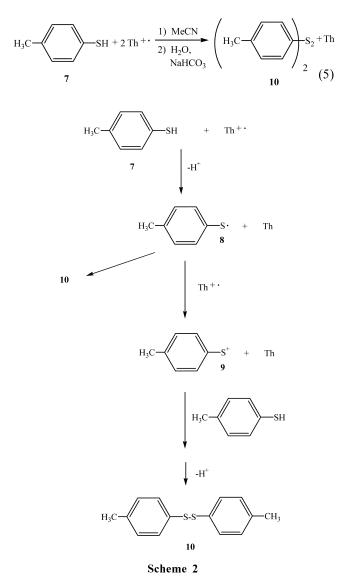
A minor one of the transformations of **2** is the formation of benzyl disulfide, **6** by coupling of free sulfur radicals (**2**) which, can also be illustrated by oxidative coupling of **1** *via* **1**$^{+\cdot}$.

Thiols are easily oxidized to disulfides by mild oxidizing agents,[22] and electrochemically.[23] However, strong oxidizing agents may give sulfonic acid.[24] But no trace of sulfonic acid was found in this experiment, therefore, Th$^{+\cdot}$ is a stable, but not a strong, one-electron oxidizing reagent.

Also, we have carried out the reaction of 1 : 1 Th$^{+\cdot}$/**1** stoichiometry using the same conditions. Benzyl disulfide, **6** (60%) was formed but much of the **1** still remained. Small amounts of other products were formed but were not identified.

Alternatively, thio-extrusion may be occurred from benzyl sulfur radical (**2**), not from benzyl sulfur cation (**3**), followed by ready oxidation of the benzyl radical to the benzyl carbocation. But neither bibenzyl by coupling of the benzyl radicals nor addition of benzyl radical to cation radical was found. Therefore, thio-extrusion from **2** can be excluded completely and thereby scheme 1 deserves rationale.

4-Methylbenzenethiol (7). Products of this reaction of **7** with Th$^{+\cdot}$ were *p*-tolyl disulfide and Th. The stoichiometry of the reaction is shown in eq 5 and the results are given in Table 1. The detailed mechanism can be understood as shown in Scheme 2.

$$\text{(5)}$$

Scheme 2

The product balances for the reaction of 2 : 1 $Th^{+\cdot}/7$ stoichiometry account for 88% of 4-methylbenzenethiol and 98% of the cation radicals. The *p*-tolyl sulfur radical, **8** was generated by a one-electron transfer of **7** to $Th^{+\cdot}$, followed by proton loss. We can imagine the formation of *p*-tolyl disulfide (**10**) as taking place in two different mechanisms shown in Scheme 2. Second oxidation of **8** by another cation radical leads to *p*-tolyl sulfur cation **9**, which reacted with **7** to form **10**. In addition, some *p*-tolyl sulfur radicals (**8**) escape oxidation and dimerize to form **10**, which also can be illustrated by oxidative coupling of **7**. However, in the oxidation of **7**, the thio-extrusion was not observed from **9**. It is evident that *p*-tolyl cation can't be formed because of its instability, and thereby carbocationic chemistry can't be observed. From the reaction of 1 : 1 $Th^{+\cdot}/7$ stoichiometry **10** (20%) was formed but a large quantity of **7** did not react. Further separation of the products and a thorough assay was not pursued. It is unclear which pathways, second oxidation of **8** with $Th^{+\cdot}$ or the combination of **8**, played a major role in the formation of **10**. The results presented here, however,

indicate that these two possibilities deserve consideration as major routes together.

Experimental Section

Thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) was prepared from thianthrene (Fluka) as described earlier.[25] The thianthrene was first purified on a column of silica gel followed by crystallization from acetone. An iodometric assay gave a $Th^{+\cdot}$ content in the range 96-99%. Acetonitrile (Aldrich, anhydrous grade) was dried by distillation from P_2O_5 under Ar. The following columns were used for GC analyses, with a Model CP-3800 Varian Inc. FID detector gas chromatograph and Varian Star #1 computer integrator, CP-Sil 5CB capillary, 15 m × 0.25 mm. Quantitative analyses were performed using authentic compounds and naphthalene as an internal standard. A response factor was measured for each authentic compound and was used for analyses in a standard way. Mass spectra, for identification of products, were measured with a Hewlett-Packard instrument, Model 5973 MSD, and Varian Inc., Model 1200, in both GC and direct-insertion-probe modes at the Seoul and Gwangju branches of the Korea Basic Science Institute. Thiols and all products, unless otherwise stated, were purchased from the Aldrich Chemical Company.

Reactions of $Th^{+\cdot}ClO_4^-$ with Aromatic Thiols. A general procedure was adopted. Thiol (0.50 mmol) and $Th^{+\cdot}ClO_4^-$ (315 mg, 1.00 mmol) were placed in a 50 mL rounded-bottomed flask, containing a stirring magnet bar. The flask was purged with dry argon after being capped with a septum. Dry acetonitrile was introduced into the flask by syringe, and the dark purple color of **1** disappeared, but the mixture was stirred overnight. Thereafter, 10 mL of water was added followed by aqueous $NaHCO_3$ to neutralize $HClO_4$ that had been formed in reaction. The solution was extracted with 3 × 30 mL portions of methylene chloride. The methylene chloride solution was dried over $MgSO_4$, and evaporated. The residue was dissolved in 10 mL of methylene chloride. Portions of this solution were used for identification of products by GC/MS and for quantitaitve analysis by GC.

N-Benzylacetamide (**8**)[26] were prepared as described in the literature.

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