Activation of Thiophenes by Superacids: Protonation and Polymerization

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Two aspects of thiophene chemistry are of current interest in materials chemistry. Polythiophenes are under intense study for possible applications in electronics and photonics, and metal–thiophene interactions are relevant to the catalytic hydrodesulfurization (HDS) process. This communication presents studies at the interface of these otherwise distinct topics, resulting from an examination of the interaction of TiCl4 with thiophenes.

We have found that CH2Cl2 solutions of HCl and TiCl4 readily protonate tetramethylthiophene to give salts of [2-HC4Me4S]+. 1H and 13C NMR analysis of these solutions indicate that protonation occurs at the 2-position. In the 1H NMR spectrum, all four C7 signals are well resolved, two of which are coupled to the unique proton in accord with similar results using more conventional superacids. From these solutions we obtained single crystals of [2-HC4Me4S]+[Ti2Cl9]−, thus allowing the first structural analysis of a protonated thiophene (Figure 1). The reflection data refined well, allowing for the identification of the unique H-atom position. The [2-HC4Me4S]+ cation features a tetrahedral carbon, C2, connected to C3 and S via bond lengths closer to values for single bonds, 1.474(7) and 1.804(5) Å, respectively. The C2–C3–C4–S sequence displays a diene-like alternation in bond lengths. The C4–S distance of 1.673(5) Å is shorter than in thiophene (1.71 Å), indicative of an enhanced S–C π-interaction. The Ti2Cl9− anion is unexceptional, consisting of a cofacial biotahedral arrangement. There is one short Cl···H interaction between a terminal chloride on the anion and the unique hydrogen.

Figure 1. Structure of [2-HC4Me4S]+[Ti2Cl9]−. Principal bond lengths (Å): S–C(1), 1.804(5); C(1)–C(2), 1.474(7); C(2)–C(3), 1.370(7); C(3)–C(4), 1.405(7); C(4)–S, 1.673(5).
solutions of C₄Me₄S are treated with excess TiCl₄ at low temperatures. Addition of hexanes to these solutions precipitates analytically pure red crystals of [(η⁵-C₄Me₄S)TiCl₃][Ti₂Cl₉⁻].³ This species is unstable in solution and decomposes upon prolonged exposure to a vacuum, indicative of its reversion to TiCl₄ and C₄Me₄S. NMR studies show that solutions of this salt react with HC1 to give the aforementioned [2-HC₄Me₄S]Ti₂Cl₉. This experiment illustrates the competition between TiCl₃⁺ and H⁺ for the weakly basic heterocycle (eq 1).

\[
\text{[TiCl₄]} + \text{HC1} \rightarrow \text{[HC₄Me₄S]Ti₂Cl₉} \quad \text{(1)}
\]

Given the successes with the C₄Me₄S/TiCl₄/HCl system, we have investigated the corresponding chemistry of the parent thiophene. Previous studies, beginning with the discovery of thiophene,¹⁰ had shown that thiophene was sensitive to strong acids to give insoluble "polymers" as well as trimERIC and tetramERIC species.¹¹ Dichloromethane solutions of thiophene and TiCl₄ (0.6 M) react to give yellow solutions. Attempts to isolate adducts from such solutions were unsuccessful; evaporation of the solution left no residue, indicating that [(C₄H₄S)TiCl₃][Ti₂Cl₉⁻], if it forms, is less stable than the C₄Me₄S derivatives. Addition of gaseous HCl to this TiCl₄/C₄H₄S solution at −78 °C, followed by warming to room temperature, led to a darkening of the solution and the formation of a brilliant red precipitate. Similar reactions can be conducted without solvent using only thiophene and TiCl₄, in which case the addition of HCl converts the solution into a red paste. Water discharges the red color, giving a yellow precipitate. Extraction of this solid with CH₂Cl₂ (CS₂ and benzene can also be used) followed by addition of hexanes to the organic phase affords a pale yellow solid (mp 145–151 °C) analyzing as C₄nH₄nSₙ.¹² The polymerization is more conveniently conducted using HOTf instead of gaseous HCl. For example starting with 3.6 g of thiophene and 4.3 g of TiCl₄ followed by the addition of HCl gave 2.5 g of polymer.

Size exclusion chromatographic (SEC) analysis showed that the solid has a number-average molecular weight (Mₙ) of 1800 and a weight-average molecular weight (Mₘ) of 3300. The polymer can be readily fractionated to give samples with Mₙ (Mₘ) values that range from 3500 (5000) to 1000 (1200). A Mₙ of 3500 corresponds to a degree of polymerization (dp) of 41.

The identification of the product as C₄nH₄nSₙ is supported by positive ion FAB MS data for a low molecular weight fraction which showed peaks from [1344 – n(84)]⁺ for 5 ≤ n ≤ 16, i.e., integral multiples of thiophene (Figure 2). MS/MS measurements on the [(C₄H₄S)₇]⁺ peak (m/z = 588) showed that the progression [1344 – n(84)]⁺ is not due to fragmentation but reflects the polydispersity of the sample. Also observed is a set of weaker peaks for [(C₄H₄S)₇ – H₂S]⁺ resulting from the fact that the C₄H₄S/TiCl₄/HCl reaction evolves some H₂S. The mechanism of this side reaction remains unknown.

![Figure 2. Positive ion FAB mass spectrum of C₄nH₄nSₙ (3-nitrobenzyl alcohol matrix).](image-url)
The \(^1H\) NMR spectrum of the polymer consists of two complex sets of resonances in the regions \(\delta 1.5-5.1\) and \(6.5-7.5\). These are attributed to hydrogen atoms attached to sp\(^3\) and sp\(^2\) carbon atoms, respectively. The ratio of the two regions is 3:1, favoring the aliphatic signals. The IR spectrum of the polymer also suggests a combination of sp\(^3\) and sp\(^2\) centers. The spectrum is dominated by a signal at 2930 cm\(^{-1}\) that is associated with \(\nu(\text{CH})\) for sp\(^3\) centers; \(\nu(\text{CH})\) for the sp\(^2\) centers is observed at 3066 cm\(^{-1}\) and \(\nu(\text{C-C})\) at 1449 cm\(^{-1}\). Kovacic and McFarland appear to have isolated a similar polymer via the reaction of \(\text{C}_4\text{H}_4\text{S}_4\) and \(\text{AlCl}_3\) in CS\(_2\).\(^{13}\)

The polymer structure is related to that of the thiophene trimer (2,2′,2′′-thienyl-2,4-tetrahydrothiophene) generated by the trimerization of thiophene by H\(_3\)PO\(_4\)\(^{14}\) which then attaches to sp\(^3\) and sp\(^2\) carbon atoms, respectively. The spectrum is dominated by a signal at 3066 cm\(^{-1}\) that is associated with \(\nu(\text{CH})\) for sp\(^3\) centers; \(\nu(\text{CH})\) for the sp\(^2\) centers is observed at 3066 cm\(^{-1}\) and \(\nu(\text{C-C})\) at 1449 cm\(^{-1}\). Kovacic and McFarland appear to have isolated a similar polymer via the reaction of \(\text{C}_4\text{H}_4\text{S}_4\) and \(\text{AlCl}_3\) in CS\(_2\).\(^{13}\)

The polymerization was not induced with TiCl\(_4\) or HCl/HOTf alone. For a given [HOTf], the \(M_n\) dropped strongly at [Ti]/[\(\text{C}_4\text{H}_4\text{S}\)] = 1, the influence of [HOTf] on \(M_n\) was negligible from ratios of 0.10 to 0.017. Thiophenes bearing substituents at the 2-position do not polymerize, as was demonstrated by GPC analyses of reactions with 2-methylthiophene and 2,5-dimethylthiophene. TiCl\(_4\)/HOTf mixtures react with 3-methylthiophene and 3-hexylthiophene to give oligomers with \(M_n \sim 900\) (dp \(\sim 8\)) and 700 (dp \(\sim 4\)), respectively.

The structure of \(\text{C}_4\text{Me}_3\text{HS}^+\) suggests that polymerization is initiated by protonation which converts thiophene into a carbon electrophile\(^4\) which then attacks unprotonated thiophene (eq 2).

\[\text{C}_4\text{H}_4\text{S} + \text{H}_3\text{PO}_4 \rightarrow \text{C}_4\text{Me}_3\text{HS}^+ + \text{H}_2\text{S} + \text{H}_2\text{O}\]

This scenario is also consistent with inhibition by substituents at the 2 and 5 positions, as well as the considerable stability of 2-HC\(_4\)Me\(_4\)S\(^+\). It remains uncertain if TiCl\(_4\) assists in the polymerization,\(^{15}\) but it is clear that TiCl\(_4\) binds to the growing polymer, hence the requirement for high concentrations of TiCl\(_4\). The affinity of the polymer for TiCl\(_4\) was confirmed by treating purified samples of the polymer (\(M_n = 2500\)) with TiCl\(_4\) to give the red adduct with the approximate stoichiometry of (\(\text{C}_4\text{H}_4\text{S}^+\))(TiCl\(_4\))\(_{1/3}\)).\(^{16}\) Hydrolysis of this adduct regenerated the polymer without altering its \(M_n\) or polydispersity. Tetrahydrothiophene is known to form stable adducts with TiCl\(_4\),\(^{17}\) and the coordinating ability of 2,3-dihydrothiophene has recently been demonstrated.\(^{18}\) Far-IR measurements of (\(\text{C}_4\text{H}_4\text{S}^+\))(TiCl\(_4\))\(_{1/3}\) reveal a broad band at 400 cm\(^{-1}\), typical of \(\nu(\text{TiCl}_4)\) for Lewis base adducts of TiCl\(_4\).\(^{19}\)

In summary, protonation of thiophene by the superacid system HCl/TiCl\(_4\) gives the TiCl\(_4\)-bound polymer \(\text{C}_4\text{H}_4\text{S}^+\)(TiCl\(_4\))\(_{1/3}\). This new material, while structurally complex, merits further study because of its low cost as well as its ability to bind transition metals. The polymerization mechanism implicates the formation of a protonated thiophene \(\text{C}_4\text{H}_4\text{S}^+\). This proposal finds support in our isolation of salts of HC\(_4\)Me\(_4\)S\(^+\).

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(14) Belenkii, L. I. Heterocycles 1994, 37, 2029.
(16) Anal. Calcd (found) for \(\text{C}_12\text{H}_{12}\text{Cl}_4\text{S}_3\text{Ti}\): C, 32.60 (32.77); H, 2.74 (2.76); S, 21.76 (21.34); Ti, 10.83 (9.70).