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Communications

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,¹ and metal–thiophene interactions are relevant to the catalytic hydrodesulfurization (HDS) process.^{2,3} This communication presents studies at the interface of these otherwise distinct topics, resulting from an examination of the interaction of TiCl_4 with thiophenes.

We have found that CH_2Cl_2 solutions of HCl and TiCl_4 readily protonate tetramethylthiophene to give salts of $[\text{2-HC}_4\text{Me}_4\text{S}^+]$. ^1H and ^{13}C NMR analysis of these solutions indicate that protonation occurs at the 2-position.^{4,5} In the ^1H NMR spectrum, all four CH_3 signals are well resolved, two of which are coupled to the unique

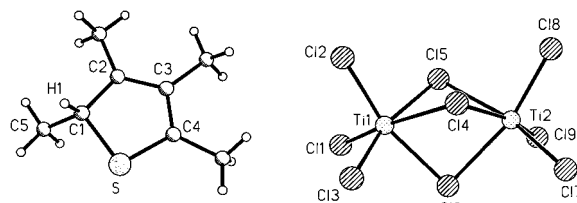


Figure 1. Structure of $[\text{2-HC}_4\text{Me}_4\text{S}^+][\text{Ti}_2\text{Cl}_9^-]$. Principal bond lengths (Å): S–C(1), 1.804 (5); C(1)–C(2), 1.474 (7); C(2)–C(3), 1.370 (7); C(3)–C(4), 1.405 (7); C(4)–S, 1.673 (5).

proton in accord with similar results using more conventional superacids.⁶ From these solutions we obtained single crystals of $[\text{2-HC}_4\text{Me}_4\text{S}^+][\text{Ti}_2\text{Cl}_9^-]$, 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.⁷ The $[\text{2-HC}_4\text{Me}_4\text{S}^+]$ 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 Ti_2Cl_9^- anion is unexceptional, consisting of a cofacial bioctahedral arrangement. There is one short $\text{Cl}\cdots\text{H}$ interaction between a terminal chloride on the anion and the unique hydrogen.

To better understand the $\text{TiCl}_4/\text{HCl}/\text{C}_4\text{Me}_4\text{S}$ reaction, we examined the interaction of $\text{C}_4\text{Me}_4\text{S}$ and TiCl_4 in the absence of acids. Floriani and co-workers had shown that hexamethylbenzene reacts with TiCl_4 to give $[(\eta^6\text{-C}_6\text{Me}_6)\text{TiCl}_3^+][\text{Ti}_2\text{Cl}_9^-]$.⁸ NMR studies suggest that the analogous $[(\eta^5\text{-C}_4\text{Me}_4\text{S})\text{TiCl}_3^+]$ is formed when CH_2Cl_2

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(5) ^1H NMR (CD_2Cl_2) δ 5.05 (m, 1H, $\text{SC}_3\text{Me}_3\text{CHMe}$), 3.09 (d, J = 3.42 Hz, 3H, $\text{SC}_3\text{Me}_3\text{CHMe}$), 2.57 (s, 3H, $\text{SC}_3\text{Me}_3\text{CHMe}$), 2.27 (s, 3H, $\text{SC}_3\text{Me}_3\text{CHMe}$), 1.87 (d, J = 7.81 Hz, 3H, $\text{SC}_3\text{Me}_3\text{CHMe}$).

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(7) For $\text{C}_8\text{H}_{13}\text{Cl}_9\text{STi}_2$: monoclinic $P2_1/n$, a = 9.441(5), b = 11.708(5), c = 18.214(13) Å, α = γ = 90°, β = 91.18(4)°, Z = 4, V = 2013(2) Å³, T = 130 K, ρ_{calcd} = 1.835 Mg/m³, for 3539 independent reflections (Mo K α ; R_{int} = 1.45%; 184 parameters refined) R_w (based on F) = 3.72% ($0.0^\circ \leq 2\theta \leq 50.0^\circ$).

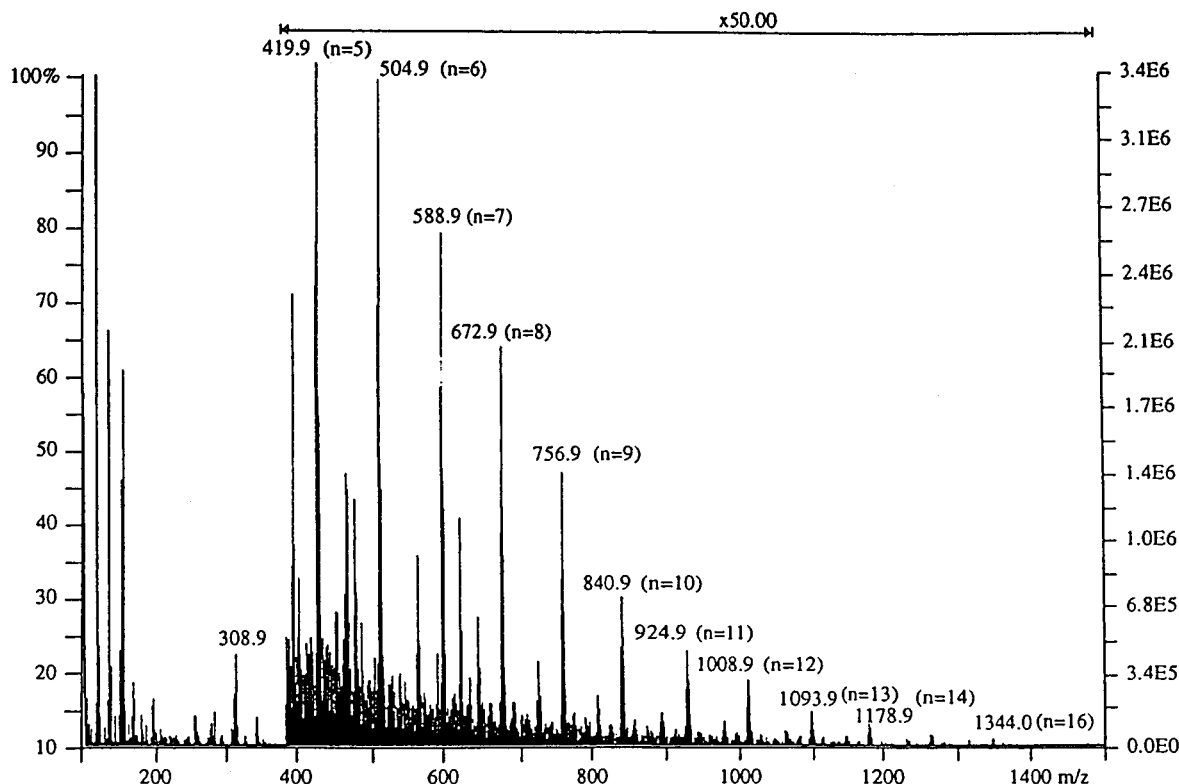
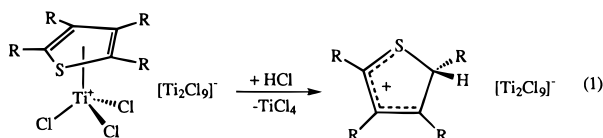


Figure 2. Positive ion FAB mass spectrum of $C_{4n}H_{4n}S_n$ (3-nitrobenzyl alcohol matrix).

solutions of C_4Me_4S are treated with excess $TiCl_4$ at low temperatures. Addition of hexanes to these solutions precipitates analytically pure red crystals of $[(\eta^5-C_4Me_4S)TiCl_3]^+[Ti_2Cl_9]^-$.⁹ This species is unstable in solution and decomposes upon prolonged exposure to a vacuum, indicative of its reversion to $TiCl_4$ and C_4Me_4S . NMR studies show that solutions of this salt react with HCl to give the aforementioned $[2-HC_4Me_4S]Ti_2Cl_9$. This experiment illustrates the competition between $TiCl_3^+$ and H^+ for the weakly basic heterocycle (eq 1).



Given the successes with the $C_4Me_4S/TiCl_4/HCl$ 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 $TiCl_4$ (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 $[(C_4H_4S)TiCl_3]^+[Ti_2Cl_9]^-$, if it forms, is less stable than the C_4Me_4S derivatives. Addition of gaseous HCl to this $TiCl_4/C_4H_4S$ solution at $-78^\circ C$, 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 $TiCl_4$, 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 CH_2Cl_2 (CS_2 and benzene can also be used) followed by addition of hexanes to the organic phase affords a pale yellow solid (mp $145-151^\circ C$) analyzing as $C_{4n}H_{4n}S_n$.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 $TiCl_4$ followed by an excess of HOTf gave 2.5 g of polymer.

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

The identification of the product as $C_{4n}H_{4n}S_n$ is supported by positive ion FAB MS data for a low molecular weight fraction which showed peaks from $[1344-n(84)]^+$ for $5 \leq n \leq 16$, i.e., integral multiples of thiophene (Figure 2). MS/MS measurements on the $[(C_4H_4S)_7]^+$ 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 $[(C_4H_4S)_n-H_2S]^+$ resulting from the fact that the $C_4H_4S/TiCl_4/HCl$ reaction evolves some H_2S . The mechanism of this side reaction remains unknown.

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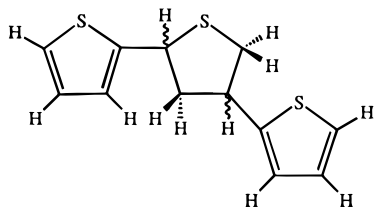
(9) Anal. Calcd (found) for $C_8H_{12}Cl_{12}STi_3$: C, 13.54 (13.74); H, 1.70 (1.74); Cl, 59.97 (59.59); S, 4.52 (4.65); Ti, 20.26 (20.24).

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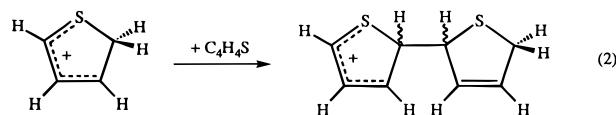
(12) Anal. Calcd (found) for $C_{4n}H_{4n}S_n$: C, 57.01 (57.10); H, 4.80 (4.70); S, 38.10 (37.90).

The ^1H NMR spectrum of the polymer consists of two complex sets of resonances in the regions δ 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 3:1.1, 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 $\nu_{\text{C-H}}$ for sp^3 centers; $\nu_{\text{C-H}}$ 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 AlCl_3 in CS_2 .¹³ The polymer structure is related to that of the thiophene trimer (2',2''-thienyl-2,4-tetrahydrothiophene) generated by the trimerization of thiophene by H_3PO_4 -clay mixtures.¹¹



Studies on the effects of stoichiometry and substituents provided additional mechanistic insights. Thiophene polymerization was not induced with TiCl_4 or HCl/HOTf alone. For a given $[\text{HOTf}]$, the M_n dropped strongly at low $[\text{Ti}]/[\text{C}_4\text{H}_4\text{S}]$, indicating that titanium is consumed in the polymerization process. For solutions where $[\text{Ti}]/[\text{C}_4\text{H}_4\text{S}] = 1$, the influence of $[\text{HOTf}]$ 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. $\text{TiCl}_4/\text{HOTf}$ mixtures react with 3-methylthiophene and 3-hexylthiophene to give oligomers with $M_n \sim 900$ ($\text{dp} \sim 8$) and 700 ($\text{dp} \sim 4$), respectively.

The structure of $\text{C}_4\text{Me}_4\text{HS}^+$ suggests that polymerization is initiated by protonation which converts thiophene into a carbon electrophile¹⁴ which then attacks unprotonated thiophene (eq 2).



This scenario is also consistent with inhibition by substituents at the 2 and 5 positions, as well as the considerable stability of $2\text{-HC}_4\text{Me}_4\text{S}^+$. 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 $(\text{C}_4\text{H}_4\text{S})_n(\text{TiCl}_4)_{n/3}$.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 $(\text{C}_4\text{H}_4\text{S})_n(\text{TiCl}_4)_{n/3}$ reveal a broad band at 400 cm^{-1} , typical of $\nu_{\text{Ti-Cl}}$ 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 $\text{C}_{4n}\text{H}_{4n}\text{S}_n(\text{TiCl}_4)_{n/3}$. 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 $\text{C}_4\text{H}_5\text{S}^+$. This proposal finds support in our isolation of salts of $\text{HC}_4\text{Me}_4\text{S}^+$.

Acknowledgment. This research was supported by the Department of Energy through DEFGO2-90ER14146 and DEFGO2-96ER45439.

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