

Oxidizing Capacity and Solvation of Copper(II) Ions in Acetonitrile: Reactivity with 2,2'-Bithiophene

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Abstract

The oxidative reactivity of some copper(II) compounds in acetonitrile was studied by the use of 2,2'-bithiophene (BT) as a testing compound. The reaction between copper(II) trifluoromethanesulfate (triflate) and BT yielded an electroconductive polythiophene triflate $[(\text{-C}_4\text{H}_2\text{S-})(\text{CF}_3\text{SO}_3)_{0.2}]_n$ with a room temperature conductivity of 0.15 S cm^{-1} , which was comparable to the conductivity of polythiophene perchlorate prepared by the reaction of copper(II) perchlorate with BT. In contrast, reactions between BT and copper(II) chloride or bromide provided halogen-substituted bithiophenes. The nitrate and trifluoroacetate did not react with BT. The reactions are strongly governed by solvation effects, which are dependent on the nature of anions in the copper(II) salts as well as on the solvent used.

Introduction

In our previous study, we reported that the sulfur-containing aromatic compound, 1,4,5,8-tetrathiafulvalene (abbreviated as TTF), is readily oxidized by copper(II) halides to form highly electroconductive charge-transfer complexes that can be represented as $[(\text{TTF})_n]^+\text{Cu}^+\text{X}_2$, in which TTF carries a fractional charge of $1/n$ [1]. One of the features of interest in these compounds is that the value of n can be controlled by the use of an appropriate solvent: the reactivity of the copper(II) compounds is regulated by solvent effects. Recently, we have extended this method (i.e. the use of cupric salts as oxidants in an appropriate solvent) to polymerization of 2,2'-bithiophene (abbreviated as BT). When copper(II) perchlorate was used as an oxidative coupling agent with BT in acetonitrile, highly electroconductive polythiophene, $[(\text{-C}_4\text{H}_2\text{S-})(\text{ClO}_4)_x]_n$ ($x \approx 0.17$) was readily obtained: the powder conductivity was 8 S cm^{-1} at 300 K [2]. In contrast, a substitution instead of polymerization occurred when copper(II) bromide was used as an oxidizing agent: 5,5'-dibromo-2,2'-bithiophene (5,5'-Br₂-BT) was obtained [3]. These findings suggested that the reactions may be governed

by the nature of the anions of the copper(II) salts as well as by the solvent. This suggestion has prompted us to carry out a systematic study of the reactivity of copper(II) compounds, although some copper(II) compounds have been used as oxidizing agents with aromatic compounds [4]. In this paper, we report the reactions between BT and copper(II) salts including chloride, bromide, nitrate, trifluoromethanesulfate (triflate) and trifluoroacetate in acetonitrile: copper(II) salts of strong acids have been studied because these salts are expected to be readily dissociated in solution so that the solvation of copper ions are effective, and BT has been used as a testing compound in the reactions because a variety of unusual chemical reactions have been found with substituted thiophenes [5]. The oxidizing capacity of the copper(II) compounds is governed by the solvation of acetonitrile, and the reaction products are markedly dependent on the nature of anions of the copper compounds used.

Results

Figure 1 summarizes the results for reactions of some copper(II) compounds with BT in acetonitrile.

The reaction between copper(II) triflate $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and BT in acetonitrile yielded a black powder, which was insoluble in organic solvents. The analytical data showed that the composition of the compound was $(\text{C}_4\text{H}_2\text{S})(\text{CF}_3\text{SO}_3)_{0.2} \cdot 0.15\text{H}_2\text{O}$, in which copper was not involved. Figure 2 shows the IR spectrum observed for the compound: a broad intense band due to an electronic transition appeared in the near IR region with a band edge at $c. 1500 \text{ cm}^{-1}$, four bands characteristic of partially oxidized polythiophene [6] were observed at 1335, 1210, 1120 and 1035 cm^{-1} , and a CH out-of-plane bending band appeared at 790 cm^{-1} . The nature of the observed spectrum is identical with that reported for electroconductive polythiophene salts [2, 6]. The electrical conductivity of the powder was 0.15 S cm^{-1} at 300 K, and the temperature dependence was explained by

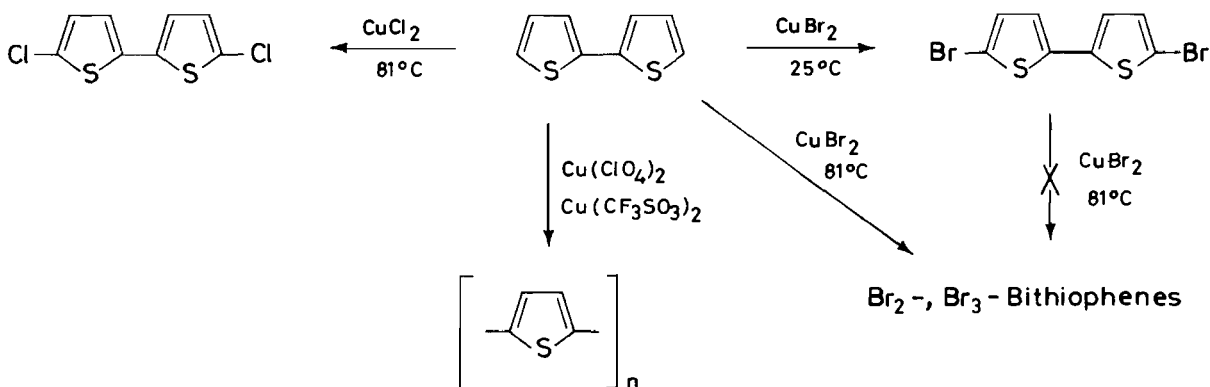


Fig. 1. Reactions between copper(II) compounds and 2,2'-bithiophene.

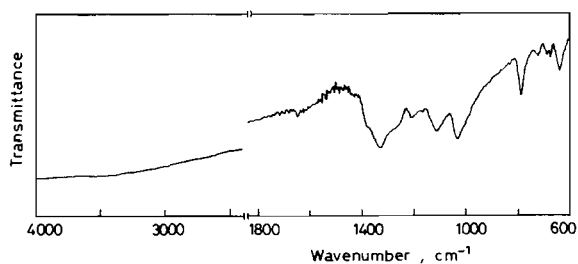


Fig. 2. Infrared spectrum of electroconductive polythiophene triflate, $[-C_4H_2S-](CF_3SO_3)_{0.2} \cdot 0.15H_2O)_n$.

$$\sigma = \sigma_{\infty} e^{-E/kT} \quad (1)$$

with the activation energy $E = 0.11$ eV at temperatures above 200 K. These experimental results evidence that BT is polymerized by the action of $Cu(CF_3SO_3)_2$ to form an electrically conducting polythiophene triflate.

The reaction between $CuBr_2$ and BT in acetonitrile at room temperature yielded 5,5'- Br_2 -BT: the melting point and the NMR spectrum agreed with those reported in the literature [7]. In the NMR spectrum, peaks attributable to other isomers were not found; the bromination proceeds selectively at the 5-carbon.

When the above reaction between $CuBr_2$ and BT was carried out in boiling acetonitrile, a number of isomers were formed: the NMR spectrum showed the peaks of 5,5'- Br_2 -BT and many additional peaks attributable to other isomers. Upon repeated recrystallization of the mixture of reaction products from hexane, light yellow prismatic crystals were obtained. Our previous X-ray study of these crystals has shown that the compound was 3,5,5'-tribromo-2,2'-bithiophene [8]. Separation of the reaction mixture on a silica gel and successive sublimation at 77 °C yielded colorless fine needles. The molecular weight was determined as 409 by vapor pressure osmometry. This value agreed with the molecular weight 403 of tribromobithiophene within the experimental error.

The 1H NMR spectrum showed two singlet peaks with the intensity ratio 1:2 at $\delta = 6.95$ (s, 1) and 7.01 (s, 2); this spectrum was different from that predicted for 3,5,5'- Br_3 -BT that had been identified by the X-ray single crystal analysis [8]. The C(5)-H protons of 2-bromothiophene derivatives exhibit an NMR peak at $\delta \geq 7$, and the C(3)-H and C(4)-H proton peaks appear at $\delta \leq 7$ [9]. Since the $I-I$ coupling due to adjacent protons was not observed, the compound is characterized as 3,4,4'-tribromo-2,2'-bithiophene. These results showed that at least two tribromo isomers were formed in the reaction. Further isolation of other isomers from the reaction mixture was unsuccessful.

5,5'- Br_2 -BT once isolated did not undergo further bromination when refluxed with $CuBr_2$ in acetonitrile, in contrast with the reaction between $CuBr_2$ and BT in boiling acetonitrile. This shows that the bromination that yields tribromobithiophenes proceeds via a mechanism that differs from that for the formation of 5,5'- Br_2 -BT. 2-Bromothiophene has been known to undergo protodebromination by the action of HBr [5]. Bromine produced in the debromination acts as a rebromination agent with thiophenes so that a number of brominated isomers are formed [5]. Upon the reaction between $CuBr_2$ and BT in boiling acetonitrile, HBr was liberated. By the action of resulting HBr, 5,5'- Br_2 -BT once produced undergoes protodebromination and successive rebromination. This results in the formation of a number of tribromobithiophene isomers. At room temperature, however, the protodebromination is suppressed in acetonitrile which is an aprotic solvent so that 5,5'- Br_2 -BT is obtained selectively.

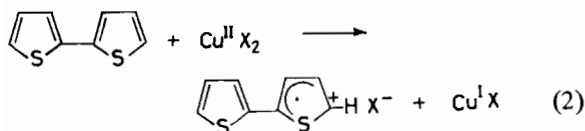
No reaction proceeded between $CuCl_2 \cdot 2H_2O$ and BT in acetonitrile at room temperature. When BT was refluxed with the chloride in acetonitrile, the known compound 5,5'- Cl_2 -BT [10] was obtained: it was confirmed by melting point and NMR data. All NMR peaks observed were attributed to 5,5'- Cl_2 -BT, indicating that the chlorination proceeded selectively at the 5-carbon.

The reaction between $\text{Cu}(\text{NO}_3)_2$ and BT in acetonitrile gave a black powder with a very low yield. The product apparently resembled the electroconductive polythiophene triflate, but it was a poor conductor with $\sigma \sim 10^{-9} \text{ S cm}^{-1}$ at room temperature. Probably, the reaction did not proceed efficiently, and only a small amount of oligomer of bithiophene was formed. The reaction of BT with the salt of a strong organic acid $\text{Cu}(\text{CF}_3\text{COO})_2$ was also studied, but no reaction occurred in acetonitrile.

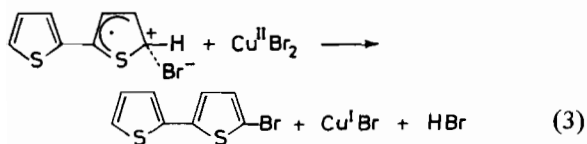
The reactions studied are summarized in Fig. 1. It is noteworthy that all reactions shown in Fig. 1 are performed only in acetonitrile; they do not occur in other common organic solvents. In tetrahydrofuran (THF), for example, BT does not react with $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ or $\text{Cu}(\text{ClO}_4)_2$. When acetonitrile was poured onto a THF solution containing the copper(II) compound and BT, however, polymerization occurred immediately at the interface between the two solvent layers, and electroconductive polythiophene salts were formed. The electrical conductivity of the products was of the same order of magnitude as that of the corresponding polythiophene salts obtained in the pure solvent. Thus, the solvation of copper ions by acetonitrile governs the course of the reactions.

Discussion

The strong solvation of copper by acetonitrile stabilizes the Cu(I) state [1, 11]. For example, $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ is stable even in air [11], whereas $\text{Cu}^{\text{I}}\text{ClO}_4$ has not been isolated. Cu(II) ions, therefore, are strong oxidizing agents in acetonitrile. In the initial state of the reaction with the copper(II) compounds, an oxidation of BT may occur as shown in eqn. (2). In the course of the reaction with CuBr_2 ,

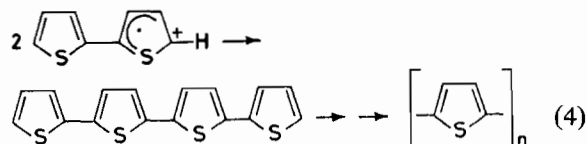


a Br^- ion produced may be coordinated to a $\text{BT}^{\cdot+}$ cation at the C(5) position due to the high nucleophilicity of bromide ions. The action of CuBr_2 against a $\text{BT}^{\cdot+}-\text{Br}^-$ complex results in the selective bromination at the 5-position. *N*-Bromosuccinimide has been reported to brominate BT and to give 5,5'- Br_2 -BT with a high selectivity [7]. Copper(II) bromide also brominates selectively the 5-carbon



of BT. In acetonitrile, the relative stability of $\text{Cu}^{\text{I}}\text{Br}$ is higher than that of $\text{Cu}^{\text{I}}\text{Cl}$ [1]. The chlorination of BT with CuCl_2 is, therefore, less efficient than the bromination.

In the reaction of BT with $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ or $\text{Cu}(\text{ClO}_4)_2$ also, $\text{BT}^{\cdot+}$ cations are formed by the action of Cu(II) ions (eqn. (2)). Triflate and perchlorate ions are hardly coordinated with $\text{BT}^{\cdot+}$ cations, because the anions have a low nucleophilicity. Instead of a substitution, therefore, a deprotonation coupling occurs between $\text{BT}^{\cdot+}$ cation radicals, and further coupling reactions lead to the formation of high polymer as shown in eqn. (4). Thus, the nucleophilicity of the anions of the copper(II) compounds is also an important factor governing the reactions with bithiophene.



The electrical conductivity of polythiophene triflate was lower than that of the corresponding perchlorate: the conductivity of $[(\text{-C}_4\text{H}_2\text{S-})\text{-}(\text{ClO}_4)_{0.17} \cdot 0.3\text{H}_2\text{O}]_n$ was 8 S cm^{-1} at 300 K and the activation energy 0.04 eV. Probably, the degree of conjugation in the polymer chains is higher for the perchlorate than for the triflate. Reactions of BT were studied also with copper(II) salts of other strong inorganic and organic acids (such as nitrate and trifluoroacetate), because these salts were expected to be readily dissociated in acetonitrile so that the solvation was strong enough to perform an oxidation of BT. On the contrary, no reaction proceeded efficiently in these systems. The oxidizing capacity of Cu(II) ions (or the stability of cuprous state by solvation) in acetonitrile is changed over a wide range depending on the counter anions even for the strong acid salts.

In conclusion, some copper(II) compounds function as excellent oxidizing agents in acetonitrile. The oxidation capacity is controlled by the solvation effect, which is governed by the nature of anions of the copper(II) compounds as well as the solvents used. The reaction products are dependent on the nature of the anions of the copper salts used as oxidants.

Experimental

Reactions Between $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and BT

A total of 206 mg (0.57 mmol) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in acetonitrile (5 ml) was added dropwise to 50 mg (0.30 mmol) of 2,2'-bithiophene in acetonitrile (10 ml) with stirring under a nitrogen atmosphere

at room temperature. After the reaction mixture was stirred for 1 h, a black powder formed, was collected on a fritted glass filter, washed with acetonitrile and dried in vacuum. The product was washed again with acetonitrile with the aid of a Soxhlet extractor to ensure the elimination of possible contaminants. Electroconducting polythiophene triflate was obtained. *Anal.* Calc. for $[(-C_4H_2S-)(CF_3SO_3)_{0.2} \cdot 0.15H_2O]_n$: C, 44.01; H, 2.00; S, 33.50. Found: C, 44.20; H, 2.08; S, 29.24% (copper was not detected).

Reactions Between $CuBr_2$ and BT

An acetonitrile solution (50 ml) containing $CuBr_2$ (2.7 g, 12 mmol) and BT (0.5 g, 3 mmol) was allowed to stand for 5 days in a closed vessel at room temperature (c. 25 °C). Nitrogen gas was passed on the resulting solution until all the solvent had volatilized. The residue was treated with water and extracted with petroleum ether. Evaporation of the petroleum ether left a light yellow crystalline powder, which was recrystallized from methanol and from hexane. The product was confirmed as 5,5'- Br_2 -BT. Yield 33%; melting point (m.p.) 143 °C; lit. m.p. 142–143 [12], 143 [13], 149–151 [7] °C. 1H NMR (CCl_4): $\delta = 6.78$ (d, 2, $J = 3.6$ Hz) and 6.92 (d, 2, 3.6 Hz), which agreed with reported data [7].

When the above reaction was carried out in boiling acetonitrile for 22 h and the product was treated in the same manner as described above, a yellow crystalline powder was obtained. The NMR spectrum showed that a number of bithiophene derivatives were formed. The product was separated on a silica gel column; hexane and cyclohexane were used successively as eluents. The first elution fraction gave a crystalline powder. The sublimation of the powder at 77 °C in vacuum gave colorless fine needles, m.p. 77–82 °C. Molecular weight determined by vapor pressure osmometry: 409; M_r of tribromothiophene = 403. *Anal.* Found: C, 23.81; H, 0.61; S, 16.28; Br, 59.75. Calc. for $C_8H_3S_2Br_3$: C, 23.85; H, 0.75; S, 15.91; Br, 59.49%. 1H NMR (CCl_4): $\delta = 6.95$ (s, 1) and 7.01 (s, 1). These data showed that the compound was 3,4,4'-tribromo-2,2'-bithiophene. Attempts to isolate other isomers were unsuccessful.

Reactions Between $CuCl_2 \cdot 2H_2O$ and BT

An acetonitrile solution (50 ml) containing BT (0.5 g, 3 mmol) and $CuCl_2 \cdot 2H_2O$ (2.2 g, 13 mmol) was refluxed for 24 h. Nitrogen gas passed on the solution to evaporate the solvent in the reaction mixture. The residue was treated with water and extracted with hexane. Evaporation of the hexane left a yellow–green powder, which was washed with

warm water and purified with the aid of a silica gel column by the use of hexane as an eluent. The product was the known compound 5,5'- Cl_2 -BT. Yield 10%; m.p. 109 °C; lit. m.p. 109 °C [10]. 1H NMR (CCl_4): a spectrum of an AB system with $\delta = 6.78$, $\Delta\delta = 0.05$ and $J = 4.8$ Hz.

Physical Measurements

The 1H NMR spectrum was recorded by the use of a Jeol JNM-PMX60SI spectrometer. The IR spectrum was obtained with a Perkin-Elmer 1420 spectrophotometer on KBr pellets. The molecular weight was determined with a Wescan 233 vapor pressure osmometry with sucrose octaacetate as the calibrant. The electrical conductivity was determined by van der Pauw's four-probe method on compressed pellets [1, 2]. Elemental analyses were performed in Huffman Laboratories, Golden, CO, U.S.A.

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