Organometallic Chemistry

Organothallium compounds. Mechanistic study of the disproportionation reaction of organothallium compounds with copper in acetonitrile

I. F. Gun'kin

Politechnical Institute, 410016 Saratov, Russian Federation

Disproportionation reactions of various phenyl- and thienylthallium dicarboxylates with copper in acetonitrile have been carried out. The reaction mechanism proposed involves the participation of the $ArTI^{2+}$ dication and various cationic pairs of the dication and the intermediate formation of organothallium radicals.

Key words: organothallium compounds; disproportionation reaction with copper; mechanism; phenylthallium and thienylthallium dicarboxylates; organothallium radicals, dications.

The disproportionation reaction of organothallium compounds is well known.¹⁻³ The most convenient methods of disproportionation use various reduction reagents.³⁻⁷ However up to now the mechanism of this reaction has scarcely been studied. Despite attempts at studying the disproportionation mechanism of organo-thallium compounds treated with trimethylphosphite,⁵ some aspects of this mechanism are not yet clear.

As a continuation of these investigations we studied the disproportionation of arylthallium dicarboxylates in acetone and revealed the crucial factors of the process.⁷ Later we showed that the disproportionation of arylthallium *bis*-trifluoroacetates is possible when they are treated with copper.⁸

We proposed two alternative mechanisms for the disproportionation of arylthallium *bis*-trifluoroacetates in acetonitrile involving the participation of the $ArTI^{\oplus}X$ (1) cation and the $ArTI^{2+}$ (2) dication, where copper acts as a one-electron reducing agent. We found that the reaction proceeds with the participation of organothallium

radical intermediates. However it was not clear which of the cations was the electron acceptor.

In order to reveal the details of this mechanism, various dicarboxylates and diphenolates of phenyl- and thienylthallium (4-10) were synthesized and the reactions of these compounds with copper in acetonitrile under various conditions were studied.

$$2 \operatorname{ArTIX}_{2} \xrightarrow{2 \operatorname{Cu}} \operatorname{Ar}_{2} \operatorname{TIX} + \operatorname{TIX} + 2 \operatorname{CuX} (1)$$

$$4-10 \qquad 4a-10a \qquad 11$$

$$\operatorname{Ar} = \operatorname{Ph}; X = \operatorname{OCOCF}_{3} (4), \operatorname{OCOCH}_{3} (5), \operatorname{OCOPr}_{i} (6), \operatorname{OCOBu}_{i} t (7), \operatorname{OC}_{6} \operatorname{F}_{5} (8);$$

Ar = 2-thienyl (9), 3-(2,5-dimethyl)thienyl (10), X = OCOCF3

Reaction (1) can be easily carried out in acetonitrile at 45°C. The structures of compounds 4a-10a were proved by microanalysis, IR and ¹H NMR spectral data. The IR and ¹H NMR spectra of compounds 4a-10a

Initial compound	Yield 4a-10a (%)	M.p./ °C (solvent)	Found (%) Calculated		Molecular formula
			С	Н	
4	79	272–274 (EA)	35.90 35.66	<u>2.38</u> 2.14	$C_{14}H_{10}F_{3}O_{2}T_{1}$
5	80	257–261 (benzine–DCE)	<u>40.53</u> 40.26	<u>3.02</u> 3.14	C ₁₄ H ₁₃ O ₂ Tl
6	90	248-250 (DCE)	<u>43.54</u> 43.02	<u>3.53</u> 3.84	C ₁₆ H ₁₇ O ₂ Tl
7	95	259–263 (MeCN)	<u>44.83</u> 44.42	<u>4.00</u> 4.17	C ₁₇ H ₁₉ O ₂ Tl
8	82	252–255 (MeCN)	<u>39.41</u> 39.91	2.22 1.86	$C_{18}H_{10}F_5OTI$
9	65	213-219 (EA-DCE)	<u>24.93</u> 24.85	<u>1.40</u> 1.25	$C_{10}H_6F_3O_2S_2TI$
10	72	160-167 (EA)	<u>30.80</u> 31.15	<u>2.69</u> 2.61	$C_{14}H_{14}F_{3}O_{2}S_{2}T_{1}$

Table 1. Disproportionation reaction (1) of organothallium compounds in acetonitrile

Note: EA - ethyl acetate, DCE - 1,2-dichlorethane

are identical to those described earlier in the Ref. 7. ¹H NMR spectra of the new compounds are given in the experimental section.

It was found that reaction (1) proceeds in a different manner depending on the temperature. If reaction (1) is carried out at room temperature or with mild heating (45°C) in argon, the reaction mixtures remain colourless. Only after oxygen penetrates into the reaction mixture, for example during filtration, or when the reaction is carried out in the air, does the colour of the reaction mixture turn bluish-green. This points out the fact that copper in the reaction mixture in the absence of oxygen is univalent (11), and in the presence of oxygen it is oxidized to Cu^{2+} .

When reaction (1) is carried out at a higher temperature (80°C) in an argon atmosphere, the colour of the reaction mixture becomes blue. Under these conditions the thermal disproportionation of compound 4 is observed, diphenylthallium trifluoroacetate 4a and thallium(III) trifluoroacetate (12) appear in the solution, and the latter reacts immediately with copper to give copper(II) trifluoroacetate (13) and thallium(I) trifluoroacetate (14).

$$2 \operatorname{ArTIX}_{2} \xrightarrow{\Delta} \operatorname{Ar}_{2} \operatorname{TIX} + \operatorname{TIX}_{3}$$
(2)

4a

4

12

$$TIX_{3} + Cu \longrightarrow TIX + CuX_{2}$$
(3)
14 13

This observation is confirmed by the fact that refluxing phenylthallium *bis*-trifluoroacetate 4 in acetonitrile solution for a long period of time results in the formation of the compound 4a, while the reaction of thallium trifluoroacetate 12 with copper in acetonitrile containing some trifluoroacetic acid yields the compounds 13 and 14.

Therefore, in order to exclude processes (2) and (3), the reactions were carried out at 45° C in an argon atmosphere. In this case, a change of the reaction mixture colour to blue or bluish green indicates the state of the copper ions, as well as the route of the disproportionation of compound **4**.

In this reaction copper is a reducing agent.⁸ Taking into account the results of Ref. 9, which showed that $(C_6F_5)_2$ TlBr disproportionates when treated with copper in dioxane, it could be proposed that the reaction products **4a-10a** should also react partially with copper.

It was found, however, that compound 4a does not react with copper: after refluxing in acetonitrile for 5 h the initial compounds, *i.e.*, 4a and copper, were quantitatively isolated. Under the same conditions thallium(I) trifluoroacetate (14) is not reduced by copper either. Thus, in reaction (1) copper does not react with the reaction products and is consumed only in the reaction with compounds 4-10. Subsequently it was shown that no matter how much of dispersed copper was used (from 2 to 50 mole excess), in reaction (1) only the amount of copper equimolecular to that of phenylthallium *bis*-trifluoroacetate 4 is consumed. Thus, the equimolecular consumption of the initial compounds in reaction (1), as well as the formation of univalent copper when the reaction is carried out at 45°C, provide indirect evidence for the one-electron character of this reaction.

Arylthallium dicarboxylates are known to be able to exist in solution as neutral molecules 4-10, various forms of ionic pairs, and to some extent as solvated ions.¹⁰ In order to find out the nature of the species participating in reaction (1), disproportionation of compound 4 in the presence of various amounts of $CF_3COO^$ ions was studied. The addition of potassium trifluoroacetate (15) or tetrabuthyl ammonium trifluoroacetate (16) to the reaction mixture results in some decrease in the reaction rate. Nevertheless, even if a 37 mole excess of 15 or 100 mole excess of 16 (relative to 4) is taken, reaction (1) does not stop, and if it is carried out for a long time (150 h), disproportionation still occurs. In this case the decrease in the reaction rate is probably caused by the shift of the ionic equilibrium towards neutral molecules 4, and, as for a large excess of 15 or 16, an additional reason is the formation of complexes of CF_3COO^- ions with molecules 4. The resulting complexes PhTIX₃⁻ have low reactivity and should generally decrease the rate of reaction (1). Previously we noted the formation of this type of complex in the exchange reactions of 5 with tetramethyltin in the presence of tetrabuthyl ammonium acetate.¹¹

Our previous investigations^{12,13} of the electrochemical reduction of organothallium compounds by the cyclic volt-ampere method make it possible to advance a proposal about the nature of the reactive species in reaction (1).

 Ph_3Tl is reduced in acetonitrile at $E_p = -1.86$ V, and reduction of diphenylthallium trifluoroacetate 4a proceeds in two stages, at $E_p = -1.01$ V and $E_p = 1.86$ V, respectively.^{12,13} At the first stage **4a** is reduced to the Ph₂Tl[•] radical, which then immediately disproportionates into Ph₃Tl and Tl. Reduction of phenylthallium bistrifluoroacetate 4 proceeds in a complicated way, but it is possible to distinguish clearly a number of stages in this process. At the first stage 4 is reduced to dication 2 at $E_{\rm p} = -0.15$ V. Subsequently, disproportionation of the reduced species occurs. At $E_p = -0.80$ V cation 1 and its ionic pairs are being reduced. Reduction of 14 is observed in acetonitrile at $E_p = -0.64 \text{ V.}^{12,13}$ Taking into account the results of orches we have into account the results of cyclic voltammetry and the fact that 4 and 14 do not react with copper, it should be recognized that in the case of 4, the species reduced at the comparatively negative potential (-0.64 V), can not cause the disproportionation reaction. The cation TI^+ is reduced at a platinum electrode in acetonitrile at $E_{\rm p}$ = -0.64 V, but it is not reduced by cooper. Therefore in the case of 4 the species reduced at $E_{\rm p} = -0.15$ V is responsible for the disproportionation in reaction (1). This is the same species that is the electron acceptor in the reaction (1).

We have ascribed¹³ to this species the structure of dication 2. Since reaction (1) still proceeds in the

presence of an excess amount of CF_3COO^- ions, which bind ions 2 into neutral molecules and thus make it impossible for them to exist, it should be recognized that disproportionation occurs also with participation of ionic pairs of the dication $[2, 2X^-]$ and $[2, X^-]^+$. It has been shown¹³ that the height of the dication 2 peak is extremely sensitive to the addition of CF_3COO^- ions. The addition of CF_3COO^- may result in the complete elimination of this peak, which is evidence of the ions 2 transformation into corresponding ionic pairs and neutral molecules.

Thus, it is possible to represent the mechanism of the disproportionation of 4 as follows (scheme 1).

According to the scheme 1 phenylthallium bistrifluoroacetates dissociates by steps, yielding cation 1 and dication 2, and also forming their ionic pairs. Copper reacts with dication 2 or with its ionic pairs to give unstable radical species including divalent thallium. These intermediate species rapidly disproportionate further to Ph_2TI^+ and TI^+ .

Reaction (1) was extended to various phenylthallium dicarboxylates. It turned out that dicarboxylates 5–7, derivatives of carbonic acids that are weaker than trifluoroacetic acid, disproportionate analogously in the presence of copper yielding diphenylthallium dicarboxylates 5a-7a (table 1).

The acidity of pentafluorophenol $(pK_a = 5.5)$ is comparable to that of carbonic acids. Therefore, the corresponding phenylthallium diphenolate **8** should be ionized to about the same extent in acetonitrile solution, and should therefore enter reaction (1). It was found that under the same conditions **8** reacts with copper to give diphenylthallium pentafluorophenolate (**8a**) (Table 1).

An investigation of reaction (1) with a series of heterocyclic organothallium compounds was carried out. It was shown that thienyl-2- and (2,5-dimethyl)-thienylthallium *bis*-trifluoroacetates (9, 10) readily react with copper yielding similar disproportionation prod-

Scheme 1

$PhTIX_2 \implies PhTIX, X$	← PhTIX	+ X	$E_{\rm p} = -0.80 \ \rm B$
$PhTI^{2+}_{X, X} \xrightarrow{\sim} PhTI^{2+}_{2, X} \sim$	$\frac{1}{2^{+}} + 2\tilde{X}$	į	$E_{\rm p} = -0.15 \ {\rm B}$
PhTI ²⁺ , $2X^{-}$ PhTI ²⁺ , X^{-} + 3 Cu PhTI ²⁺		PhTI ⁺ X ⁻ PhTI ⁺ , X ⁻ PhTI ⁺	+ CuX + Cu ⁺ + Cu ⁺
2 PhTI ⁺ , Х <u>быстро</u> 2 PhTI ⁺ <u>быстро</u>	$Ph_2TIX + Ph_2TI^+ +$	TIX TI ⁺	

ucts (9a, 10a). These results show that the process is determined mostly by the thallium center in 4-10, since it alone accepts an electron from copper.

Thus, disproportionation reactions of phenyl- and thienylthallium dicarboxylates have been carried out, and the probable reaction mechanism has been discussed.

Experimental

IR spectra were recorded on a «UR-20» spectrophotometer in vaseline oil and hexachlorbuthadiene, ¹H NMR spectra were taken on a «Varian-80» spectrometer (60 MHz) in DMSO- d_6 . Absolute acetonitrile was used in the reactions.

Phenylthallium dicarboxylates 4–7 were obtained by the reaction of phenylthallium(III) hydroxide with the corresponding carbon acids.¹⁴ Thienyl-2-thallium *bis*-trifluoroacetate 9 was obtained by the known procedure.¹⁵ Phenylthallium dipentafluorophenolate 8 was synthesized by the reaction of phenylthallium(III) hydroxide with a double amount of pentafluorophenol in refluxing benzene analogously with the procedure given in ref. 14. Active copper powder was obtained by the known procedure.¹⁶. The powder was stored in water, and immediatly before the experiment it was washed with dilute H_2SO_4 , weak solution, water, and acetone and dried in a vacuum at 50 °C.

Disproportionation of phenylthallium dicarboxylates 4–7 by the copper powder in acetonitrile (general procedure, given for the example of phenylthallium bis-trifluoroacetates 4). Copper (1.27 g, 20 mmol) was added to a solution of 2.44 g (4.81 mmol) of 4 in 20 ml of acetonitrile, and argon was bubbled into this heterogeneous mixture for 15 min. The mixture was stirred with a magnetic stirrer in an argon atmosphere at 45 °C for 8 h. Then the unreacted copper was filtered off and washed with warm acetonitrile in argon to give a colouless acetonitrile solution, which turned blue on contact with air. Acetonitrile was removed in a vacuum to the minimum volume, and a weak aqueous solution of trifluoroacetic acid (pH = 2-3) was added. The bluish green solid precipitate was filtered, dried, and triturated in a mortar in the presence of a weak aqueous solution of trifluoroacetic acid (pH = 3-4). This process was repeated several times, thus removing the thallium and copper salts into the solution, which turnedbluish green, while the precipitate turned white. The characteristics for diphenylthallium trifluoroacetate 4a and for compounds 5a-10a are given in table 1. The ¹H NMR and IR spectra of the compound isolated were identical to those reported previously⁷.

The reactions of 4 with copper in the presence of salts of 15 or 16 were carried out in a similar way. The amounts of salts added varied from a 4 to 100 molar excess relative to 4. Accordingly, the time necessary for the completion of the reaction, became longer (from 10 to 150 h).

The other phenylthallium dicarboxylates 5-7 are less soluble, so the reaction was carried out in a considerable amount of acetonitrile. The resulting phenylthallium dicarboxylates 5-7 are sparingly soluble in CH₃CN, and so partially precipitated. 5a-7a were isolated from the acetonitrile solution by the procedure described above, while the precipitate was extracted with hot acetonitrile or some other suitable solvent (DMF) and separated from copper. The isolated compounds were recrystallized. Results are given in Table 1. ¹H NMR and IR spectra of the compound obtained were identical to those reported previously⁷.

Di(thienyl-2)-thallium trifluoroacetate (9a). 9a was obtained by disproportionation of 9 in acetonitrile, m.p. 213–219 °C (from ethyl acetate—dichlorethane, 2:1). Microanalysis data are given in Table 1. ¹H NMR spectrum (DMSO-d₆, δ , ppm, J, Hz): 7.34 (d, H(4), $J_{TI-H(4)} = 106.92$), 7.45 (d, H(3), $J_{TI-H(3)} = 306.92$), 7.89 (d, H(5), $J_{TI-H(5)} = 194.97$). Di(2,5-dimethyl)thienyl-3-thallium trifluoroacetate (10a).

Di(2,5-dimethyl)thienyl-3-thallium trifluoroacetate (10a). 10a was obtained by disproportionation of 10, m.p. 160– 167°C (from acetonitrile). Microanalysis data are given in Table 1. ¹H NMR spectrum (DMSO-d₆, δ , ppm, J, Hz): 250 (s, 6H, CH₃), 6.84 (d, H(4), J_{T1-H(4)} = 123.09).

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