Organothallium compounds. Study of the iodination of dibutylthallium salts by molecular iodine in dioxane

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The kinetics of the reaction of dibutylthallium salts with iodine in dioxane were studied. The reaction rate depends appreciably on illumination, and the process as a whole is photochemical. The contribution of the dark reaction is insignificant. The reactivity of dibutylthallium salts depends on the counterion and changes in the following order: $Bu_2TlBF_4 < Bu_2TlOCOCF_3 < Bu_2TlOAc < Bu_2TlCl < Bu_2TlBr < Bu_2TlOOCPr^i$. A radical mechanism for the reaction was proposed.

Key words: organothallium compounds, kinetics, mechanism, iodine, dibutylthallium salts, iodination.

Halogenation of organometallic compounds is one of the best known reactions.[1] The mechanisms of iododemercuration[1] and iododestannation[2,3] have been studied in most detail. The mechanism of the reactions of organothallium compounds with halogens has not yet been studied.

The cleavage of the thallium—carbon bond was accomplished for the first time by treatment of dialkylthallium bromides with Br_2 in pyridine.[4] It has been shown that organothallium compounds (**1**) of the aromatic series can be iodinated with iodine in chloroform.[5,6]

However, all these studies have been scattered, and no systematic investigation of the halogenation of compounds **1** has been carried out so far. We synthesized various salts of dibutylthallium[7,8] and studied systematically their iodination with molecular iodine in dioxane.

Results and Discussion

The reactions of dibutylthallium salts with iodine on exposure to light were studied. The reaction of dibutylthallium tetrafluoroborate (**2**) with iodine at a low illumination intensity (L = 50 lx) in boiling diethyl ether in the presence of air proceeds slowly to give 1-iodobutane and thallium(I) tetrafluoroborate (**3**).

$$\underset{\mathbf{2}}{\mathrm{Bu_2TlBF_4}} + \mathrm{I_2} \longrightarrow \mathrm{2BuI} + \underset{\mathbf{3}}{\mathrm{TlBF_4}} \qquad (1)$$

Reaction (1) occurs under heterogeneous conditions due to the poor solubility of compound **2**.

However, when the reaction is carried out in dioxane under homogeneous conditions and under more intense illumination (L = 15000 lx) in an argon atmosphere, TlI (**4**) is formed along with **3**.

$$\underset{\mathbf{2}}{\mathrm{Bu_2TlBF_4}} + \mathrm{I_2} \xrightarrow[\text{Dioxane}]{h\nu,\ \text{Ar}} \mathrm{BuI} + \underset{\mathbf{3}}{\mathrm{TlBF_4}} + \underset{\mathbf{4}}{\mathrm{TlI}} \qquad (2)$$

The molar ratio of salts **3** and **4** resulting from reaction (2) is ~1 : 1.

Thus, iodination of compounds **1** differs from similar reactions of organomercury or organotin compounds in that thallium is reduced during the reaction.

Having obtained these results, we studied the kinetics of reactions (1) and (2) in dioxane by following the change in the optical density of iodine (λ_{max} 530 nm).

When the concentrations of the reactants ($C_0 = 1.5 \cdot 10^{-3}$ mol L^{-1}) are equal, iodination in the presence of air is retarded. As the reaction proceeds, an absorption maximum with λ 430 nm appears. The retardation of reaction (1) in dioxane may be due to the following reasons: (1) the effect of oxygen on the photochemical radical process; (2) the formation of complexes during the reaction. However, when reaction (1) is carried out in the dark and, hence, no radical species are formed and the effect of oxygen is slight, it nevertheless slows down. Therefore, we attributed the retardation of reaction (1) and the appearance of the absorption maximum at 430 nm to the complexation of molecular iodine with the intermediate organothallium derivative and with compound **4** according to Eqs. (3) and (4).

$$\mathrm{BuTlXI} + \mathrm{I_2} \longleftrightarrow \mathrm{BuTlXI_3} \qquad (3)$$

$$\underset{\mathbf{4}}{\mathrm{TlI}} + \mathrm{I_2} \longleftrightarrow \mathrm{TlI_3} \qquad (4)$$

This assumption is confirmed by the fact that when tetrabutylammonium iodide is added to a dioxane solution of iodine, the maximum at 430 nm appears, and the rate of reaction (1) decreases. A similar maximum at

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Table 1. Rate constants of iodination of dibutylthallium tetrafluoroborate with iodine in dioxane in the presence of air under illumination with intensity L = 4000 lx

Entry	$C_0 \cdot 10^3$/mol L^{-1}		T/°C	$k_1 \cdot 10^2$/min^{-1}
	Bu_2TlBF_4	I_2		
1	1.5	1.5	20.6	Retardation
2	5.0	0.5	20.6	1.94
3	12.5	0.5	20.6	1.84
4	25.0	0.5	20.6	1.89
5	12.5	0.5	15.0	1.45
6	12.5	0.5	25.0	2.38
7	12.5	0.5	30.0	2.67
8	25.0	0.47	35.0	3.66

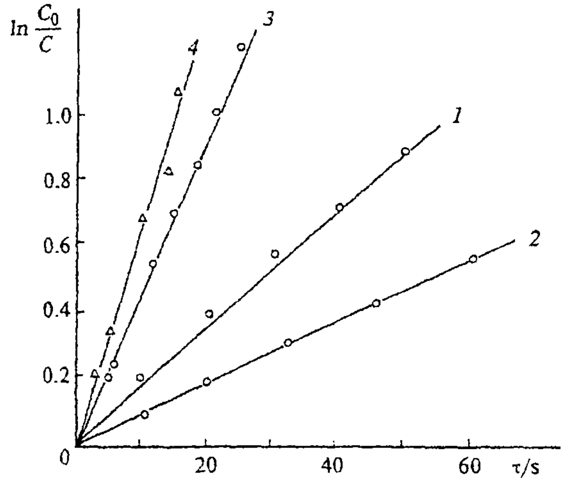


Fig. 1. Anamorphoses of the kinetic curves for the reaction of dibutylthallium salts with iodine in dioxane at identical illumination intensities (L = 4000 lx) under various conditions: $[Bu_2TlBF_4]_0 = 2.5 \cdot 10^{-2}$ mol L^{-1}, $[I_2]_0 = 5 \cdot 10^{-4}$ mol L^{-1}, in air, T = 20.6 °C (*1*); $[Bu_2TlBF_4]_0 = 1.25 \cdot 10^{-2}$ mol L^{-1}, $[I_2]_0 = 5.7 \cdot 10^{-4}$ mol L^{-1}, $[Bu_4NI] = 3 \cdot 10^{-4}$ mol L^{-1}, in air, T = 20.6 °C (*2*); $[Bu_2TlBF_4]_0 = [I_2]_0 = 1.5 \cdot 10^{-3}$ mol L^{-1}, under argon, T = 25 °C (*3*); $[Bu_2TlOCOCF_3]_0 = [I_2]_0 = 1.5 \cdot 10^{-3}$ mol L^{-1}, under argon, T = 25 °C (*4*).

430 nm appears upon dissolution of compound **4** in a solution of I_2 in dioxane. The formation of the I_3^- complex has also been observed previously in the iodination of organometallic compounds.[1–3] However, oxygen also retards reaction (1), because the same reaction carried out under argon occurs at a higher rate. Due to the retardation of reaction (1), it is impossible to calculate the rate constants of iodination under these conditions. To determine the possibility of calculating the rate constant of the iodination according to reaction (1), we studied this reaction under pseudo-unimolecular conditions when [**2**] ≫ $[I_2]$ (Table 1).

We found that at large concentrations of compound **2** ($C_0 \approx 2 \cdot 10^{-2}$ mol L^{-1}) in the presence of air, virtually no retardation of the reaction occurs. The variation of the concentration of iodine (see Table 1) is described by a first-order equation. The calculated first-order rate constants are listed in Table 1. However, when the degree of conversion is large (80—90%), reaction (1) is somewhat retarded.

When reaction (1) is conducted under pseudo-unimolecular conditions with [**2**] >> $[I_2]$, the absorption maximum at 430 nm does not appear but, instead, a maximum at 370 nm is observed. We attributed this maximum to the formation of compound **4** during reaction (1).

Varying the concentration of compound **2** in the $2.5 \cdot 10^{-2}$—$5 \cdot 10^{-3}$ mol L^{-1} range does not markedly change the rate constant of iodination (see Table 1). The semilogarithmic anamorphoses of the corresponding kinetic curves are shown in Fig. 1 (straight lines *1, 2*).

The activation energy of the reaction found from the dependence of $\log k_1$ on $1/T$ is equal to 35.7 kJ mol^{-1}.

The following scheme for the interaction of dibutylthallium salts with iodine in dioxane on exposure to light can be proposed:

$$I_2 \xrightarrow{h\nu} 2\,I^{\cdot}, \qquad \text{(a)}$$

$$R_2TlX + I^{\cdot} \longrightarrow RI + RTl^{\cdot}X, \qquad \text{(b)}$$

$$2\,RTl^{\cdot}X \xrightarrow{\text{Fast}} R_2TlX + TlX, \qquad \text{(c)}$$

$$RTl^{\cdot}X + I^{\cdot} \longrightarrow RTlXI, \qquad \text{(d)}$$

$$RTlXI + I_2 \longleftrightarrow RTlXI_3, \qquad \text{(e)}$$

$$RTlXI \longrightarrow RI + TlX, \quad RTlXI \longrightarrow RX + TlI, \qquad \text{(f)}$$

$$TlI + I_2 \longleftrightarrow TlI_3, \qquad \text{(g)}$$

$$RTlXI_3 \longrightarrow RI + TlX + I_2. \qquad \text{(h)}$$

According to the above scheme, an iodine molecule absorbs a quantum of light and decomposes into two iodine atoms (a). An iodine atom attacks the starting compound **1** at the carbon—thallium bond, leading to its homolytic cleavage (b). The intermediate organothallium radical thus formed rapidly disproportionates to give the initial **1** and TlX (c). Disproportionation of organothallium compounds has been observed previously.[9,10]

The organothallium radical contains a divalent thallium ion. The disproportionation $2Tl^{2+} \longrightarrow Tl^{3+} + Tl^{+}$ occurs at a high rate equal to $2.3 \cdot 10^9$ L mol^{-1} s^{-1} (Ref. 11) *i.e.*, the radicals formed are immediately destroyed and cannot act as chain-propagating species.

The organothallium radicals generated in this process react simultaneously with iodine atoms to give RTlXI (d), which then forms a complex with molecular iodine (e) thus decelerating reaction (1). Step (e) occurs more efficiently when the reactants are present in equimolar amounts, and the reaction is retarded. The fact that at high concentrations of the organothallium derivative when $[R_2TlX] >> [I_2]$, no substantial retardation of reaction (1) in the presence of air is observed can be explained in the following way. First, when the concentration of **1** increases, the effect of oxygen is less pronounced, since a greater part of the I$^•$ radicals is trapped by molecules **1**, and, second, the effect of complex formation also decreases, because the I$^•$ radicals are trapped by molecules **1**, and, hence, step (b) occurs less efficiently. The compounds RTlXI and $RTlXI_3$ formed in the process decompose, as shown in the above-presented scheme (f, h). In order to eliminate the effect of oxygen, reaction (1) was subsequently studied in the presence of argon.

When the reaction is carried out under argon, the situation somewhat changes. Generally, the addition of an inert gas to the reaction medium during photochemical processes causes a great number of various effects, which are difficult to fully interpret.[12] However, it can be stated that in an argon atmosphere, when argon is bubbled through a dioxane solution of the reactants, the rate of iodination is 40—50 times higher than that in air. Table 2 presents the kinetic data obtained for the iodination of compound **1** with iodine in dioxane under argon. In this case, reaction (1) is not retarded at an equimolar quantities of the reactants ($C_0 = 1.5 \cdot 10^{-3}$ mol L^{-1}) up to a degree of conversion equal to 60%. The kinetic curves correspond most closely to a first-order equation. In this case, the spectrum of the reaction mixture does not exhibit a maximum at 430 nm but instead it exhibits a low-intensity band at 370 nm. The semilogarithmic anamorphoses of the corresponding kinetic curves are shown in Fig. 2. It follows from Table 2 that the rate constant of the iodination of dibutylthallium salts depends on the nature of the salt. The reactivity of dibutylthallium salts toward iodine depends on the nature of the counterion and changes in the following sequence: BF_4 < CF_3COO < AcO < Cl < Br < Pr^{i}COO.

In the series of dibutylthallium carboxylates, the reaction rate constant (k_1) increases 24-fold on going from trifluoroacetate to isobutyrate in the following order: CF_3COO < AcO < Pr^{i}COO. The degree of ionicity of the Tl—X bonds (X is the acid residue) in thallium carboxylates and, hence, the positive charge on the thallium atom decrease in the same order facilitating the abstraction of an electron from the carbon—thallium bond by iodine. From this viewpoint, it becomes clear why the iodination of compound **2** occurs at the lowest rate. In fact, among the compounds under study, this particular compound is characterized by the largest positive charge on the thallium atom.

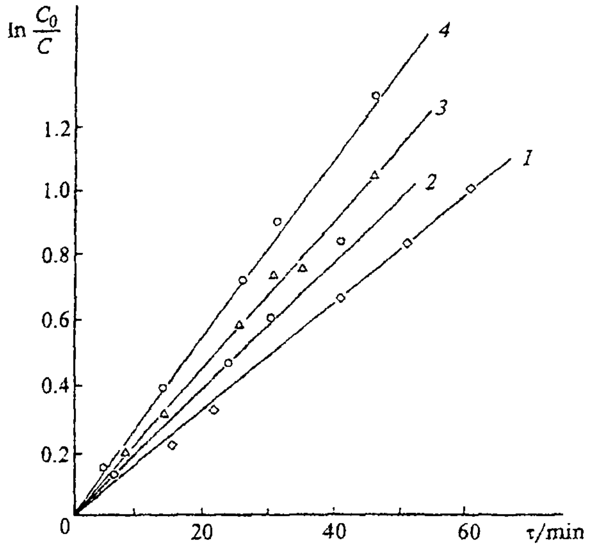
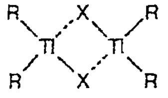


Fig. 2. Anamorphoses of the kinetic curves for the reaction of dibutylthallium salts with iodine in dioxane under argon at 25 °C at illumination intensity L = 4000 lx and at equimolar amounts of the reactants ($C_0 = 1.5 \cdot 10^{-3}$ mol L^{-1}): Bu_2TlOAc (*1*); Bu_2TlCl (*2*); Bu_2TlBr (*3*); $Bu_2TlOCOPr^i$ (*4*).

Table 2. Rate constants of iodination of dibutylthallium salts with iodine in dioxane under argon and under illumination with intensity L = 4000 lx

Compound	T/°C	$C_0 \cdot 10^3$/mol L^{-1}		k_1/min^{-1}
		Bu_2TlX	I_2	
Bu_2TlBF_4	25	1.5	1.5	0.047
$Bu_2TlOCOCF_3$	25	1.5	1.5	0.069
Bu_2TlOAc	25	1.5	1.5	1.02
$Bu_2TlOCOPr^i$	25	1.5	1.5	1.65
Bu_2TlCl	25	1.5	1.5	1.23
Bu_2TlBr	25	1.0	1.0	1.46
Bu_2TlBF_4	15	1.5	1.5	0.029
Bu_2TlBF_4	20	1.5	1.5	0.036
Bu_2TlBF_4	30	1.5	1.5	0.059
Bu_2TlCl	20	1.5	1.5	0.93
Bu_2TlCl	25	1.5	1.5	1.23
Bu_2TlCl	35	1.5	1.5	1.75

The relatively high rate of the iodination of dibutylthallium halides can be explained by coordination of the halogen to the thallium atom. Dialkylthallium and diarylthallium halides are known to form dimers in which the positive charge on the thallium atom is partly balanced due to the formation of bridging bonds.[13]



X = Cl, Br, I

A similar coordination to the thallium atom has also been found in the case of alkythallium and arylthallium dicarboxylates derived from weak carboxylic acids.[14] Therefore, the reactivities of dibutylthallium acetate and isobutyrate in iodination are comparable to those of dibutylthallium halides.

In order to confirm the scheme proposed for the reaction and its radical mechanism, we studied the reactions of dibutylthallium chloride (**5**) with iodine in dioxane at different illumination intensities. The rate constant of iodination increases linearly as the illumination intensity increases (Table 3). When irradiation is

Table 3. Rate constants of iodination of dibutylthallium chloride with iodine in dioxane under argon at 25 °C and at various illumination intensities

Entry	Illumination of the reactor/lx	$C_0 \cdot 10^3$/mol L^{-1}		k_1/min^{-1}
		Bu_2TlCl	I_2	
1	4000	1.5	1.5	1.23
2	2550	1.5	1.5	0.69
3	1050	1.5	1.5	0.29
4	290	1.5	1.5	0.18
5	50	1.5	1.5	0.02
6	0	1.5	1.5	0.001

terminated, the reaction sharply decelerates. It was found that in the dark, when the intensity of illumination is equal to zero, the rate constant of iodination (k_1) is not equal to zero. The dark reaction proceeds very slowly ($k_1 \approx 0.001$ min^{-1}), and its contribution to the process is slight. When the reactor is illuminated (L = 4000 lx), the iodination rate increases 1200-fold with respect to that of the dark reaction. Thus, under the conditions used in our experiments (L = 4000 lx), we have always observed a photochemical reaction.

Variation of the concentration of compound **1** at a constant illumination intensity (L = 4000 lx) and a constant concentration of iodine under argon demonstrates that the reaction rate depends on the concentration of **1**. Using the van't Hoff's method, we determined the order of the reaction with respect to compounds **2** and **5**. The reaction order with respect to **5** was found to be 0.6, while that with respect to **2** is 0.4. The effect of the iodine concentration on the rate of this photochemical reaction is difficult to study, because the intensity of the absorbed light varies as a function of the iodine concentration. Therefore, the reaction rate changes. This hampers the investigation of the purely concentration effect for I_2. However, we determined the order of the reaction with respect to iodine in dioxane in the presence of argon under pseudo-unimolecular conditions, *i.e.*, for [**2**] >> [I_2]. Under these conditions, the order of the reaction with respect to iodine is 1. Thus, the overall order of the iodination of dibutylthallium salts in dioxane in the presence of argon is fractional: 1.6 for compound **5** and 1.4 for compound **2**. This result indicates that this reaction actually occurs by a radical mechanism, since it is radical reactions that are normally characterized by fractional orders. Thus, the rate of iodination of dibutylthallium salts depends on numerous factors: formation of intermediate products, intensity of illumination of the reactor, the nature of the dibutylthallium salt, and the presence of air or argon in the reaction system.

We studied the kinetics and the mechanism of the reaction of dibutylthallium salts in dioxane on exposure to light and found that it occurs by a complex photochemical radical mechanism.

Experimental

Dioxane was distilled over alkali, then refluxed over sodium in the presence of benzophenone under argon until a blue solution was formed, and distilled in an argon atmosphere. In every kinetic experiment, freshly distilled dioxane was used. Iodine was purified by sublimation. The dibutylthallium salts used in this work were prepared by known procedures.[7,8] The spectra of the reaction mixtures and iodine, and the spectra in the kinetic measurements were recorded on an SF-26 spectrophotometer using 1-cm thick cells.

Reaction of dibutylthallium tetrafluoroborate with iodine in ether. Iodine (0.38 g, 1.497 mmol) in ether was added to a solution of compound **2** (0.61 g, 1.504 mmol) in 90 mL of ether stirred by a magnetic stirrer. The reaction mixture was stirred and refluxed in the presence of air in weak daylight (L = 50 lx) until it became colorless. Then the mixture was filtered to give 0.43 g (98.1%) of tetrafluoroborate **3**. The resulting salt was readily soluble in water; the addition of KI gave salt **4** as a yellow precipitate. The ethereal filtrate was concentrated to give 0.485 g (87.5%) of 1-iodobutane, b.p. 131 °C, n_D^{20} 1.4994.

Reaction of 2 with iodine in dioxane under intense illumination (L = 15000 lx) in the presence of argon. A solution of tetrafluoroborate **2** (0.2 g, 0.493 mmol) in dioxane was added in the dark to a solution of I_2 (0.125 g, 0.492 mmol) in dioxane; argon was bubbled through the mixture, and the mixture was stirred by a magnetic stirrer exposed to the light of a 150-W lamp with an illumination intensity (L) of 15000 lx. The reaction mixture became colorless over a period of 1 h, and the precipitate that formed was filtered off to give 0.14 g of a light-yellow substance, from which 0.077 g (42.2%) of compound **4** and 0.065 g (45.5%) of compound **3** were isolated.

The kinetics of reaction (1) were studied under temperature-controlled conditions in a cylindrical reactor with an external diameter of 4.1 cm and an internal diameter of 3.0 cm. A small magnetic bar was placed on the bottom of the reactor. The reactor was arranged 16 cm away from the light source. The irradiation was carried out using a 60-W tungsten lamp. The intensity of the light sorce was controlled by varying the voltage in the circuit using a transformer. The illumination intensity of the reactor was determined using a Yu-116 luxometer. When the reaction was carried out under argon, the reactor was preliminarily maintained at a constant temperature and purged with argon, then a dioxane solution of a butylthallium salt was placed into it, and argon was bubbled through the solution for an additional 15 min. Then a dioxane solution of iodine was added in the dark. The total volume of the reaction mixture was always 10 mL. After that, 3.5 mL of the reaction mixture was withdrawn in the dark, and the optical density of the solution at the beginning of the reaction was measured. The sample was returned to the reactor, the mixture was purged with argon for an additional 4 min, and the magnetic stirrer and the light source were switched on. At regular intervals, 3.5-mL samples were taken for optical density measurements. The samples were returned into the reactor. During the measurements of the optical density, the light source was temporarily switched off. In some entries, the light source was permanently operating. The rate constants obtained in these cases were within an experimental error of ±7%. When the reaction was carried out in air, the mixture was not purged with argon.

The measured optical densities of iodine at 530 nm were used to construct the kinetic curves and to calculate the rate constants for the reactions. The results are listed in Tables 1—3.

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