

## SUBSTITUTION REACTIONS IN ORGANOTHALLIUM COMPOUNDS I. EXCHANGE OF PHENYL GROUPS BETWEEN $\text{Ph}_2\text{Tl}^+$ AND $\text{Ph}_2\text{Hg}$

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### SUMMARY

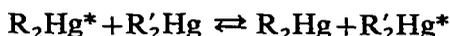
This study reports the kinetics and thermodynamic reaction parameters of the substitution reaction between  $\text{TlPh}_2^+$  and  $\text{HgPh}_2$ . A bimolecular  $S_{\text{E}i}$  transition state is proposed similar to that already proposed for mercury-aryl exchange reactions, and the relative magnitude of the activation parameters is discussed in terms of the charged species and stereochemistry of the reactants.

### INTRODUCTION

In recent years much work has been done on the substitution reactions of organometallic compounds<sup>1</sup>. The object of this work has been to elucidate the mechanism of electrophilic substitution at a saturated carbon atom. Organometallic compounds have been especially suited to this task in that the electronic arrangement confers a partial positive charge on the metal atom.

Nesmeyanov<sup>2</sup> and Ingold<sup>1</sup> have studied homogeneous mercury-aryl exchange and have proposed three mechanisms for electrophilic substitution. These mechanisms have been designated  $S_{\text{E}1}$ ,  $S_{\text{E}2}$  and  $S_{\text{E}i}$ , by analogy to nucleophilic substitution.

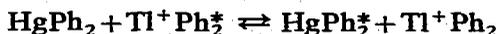
Exchange reactions of the type:



have been studied by Reutov *et al.*<sup>3</sup> and in more detail by us<sup>4</sup> and were designated as "four alkyl" reactions by Ingold *et al.*<sup>5</sup>.

Work conducted on substitution reactions in such aryl metal compounds has frequently been interpreted in terms of the  $S_{\text{E}i}$  mechanism. These reactions were fast and rigorous kinetic treatment was further hampered by the difficulty in separating the chemically similar compounds  $\text{R}_2\text{Hg}$  and  $\text{R}'_2\text{Hg}$ .

This present study has been undertaken in order to extend the information available on these "four alkyl" substitution reactions by using the species  $\text{TlPh}_2^+$  which being isoelectronic with  $\text{HgPh}_2$  would be expected to behave in a chemically similar manner, but due to its charge simplifies the chemical separation of the reaction products. This initial report is concerned with the kinetics of the reaction:



## EXPERIMENTAL

*I. Materials*

Commercially available diphenylmercury (Koch-Light Laboratories Ltd.) was recrystallised from benzene to constant melting point m.p. 123–124° Lit.<sup>6</sup> m.p. 123–124°.

Thallic chloride was prepared by passing gaseous chlorine through a suspension of thallic chloride in distilled water<sup>7</sup>. The solution of thallic chloride was concentrated, without interrupting the stream of chlorine, by heating on a water bath until crystals began to form. On cooling a solid mass of  $\text{TlCl}_3 \cdot 4 \text{H}_2\text{O}$  was obtained. The crystalline product was dissolved in ether and the solution dried over anhydrous copper sulphate.

Diphenylthallium bromide was prepared by addition of an ethereal solution of thallic chloride to the Grignard reagent of bromobenzene at 0°<sup>7</sup>. On completion of addition the reaction mixture was evaporated to dryness on a water bath. Distilled water was added and the crude product filtered off and purified by boiling with 1/1 glacial acetic acid followed by double recrystallisation from pyridine. (Found: C, 35.50; H, 2.14.  $\text{C}_{12}\text{H}_{10}\text{BrTl}$  calcd.: C, 32.87; H, 2.30%.)

<sup>14</sup>C-Diphenylthallium bromide was prepared by adding bromobenzene-<sup>14</sup>C[u] (The Radiochemical Centre, Amersham, England) to the bromobenzene used in the Grignard preparation.

Analar grade pyridine (B.D.H.) was dried over sodium hydroxide pellets and fractionally distilled, the fraction boiling between 114° and 115° being collected for use as the reaction medium.

The liquid scintillation phosphor used consisted of 6 g of DPO and 0.1 g of POPOP\* dissolved in 750 ml of dioxane, 125 ml of anisole and 125 ml of 1,2-dimethoxyethane. The dioxane, anisole and 1,2-dimethoxyethane were supplied as "scintillation chemicals" (Koch-Light Laboratories Ltd.) and required no further purification.

*II. Reaction procedure and results*

As some of the kinetic runs were to be carried out at 115° in pyridine, it was important that the reaction vessel should be designed to minimise losses due to evaporation. The vessel chosen had a long narrow neck with a ground glass stopper fitted and held firmly in place with a spring clip. The vessel was immersed in an electrically heated oil bath, thermostatted to within  $\pm 0.1^\circ$  over a range between 80° and 120°.

An aliquot of the diphenylthallium bromide in pyridine was pipetted into the reaction vessel and allowed to equilibrate, each run was then started by adding an aliquot of the diphenylmercury in pyridine. Aliquots (8 ml) of the reaction mixture were serially withdrawn and run into 100 ml of dry ether, cooled in an acetone/solid carbon dioxide bath. The precipitated diphenylthallium bromide was collected by filtering the ethereal suspension through a 1 cm circle of fine filter paper (Whatman No. 542). After washing with dry ether at room temperature the precipitate and filter paper were air dried at 100° for one hour, and cooled in a vacuum desiccator. The

\* DPO = diphenyl oxide; POPOP = 1,4-bis(5-phenyloxazolyl-2)-benzene.

dry precipitate was weighed into a tarred counting bottle, and dissolved by adding 2 ml of dimethylformamide, the precipitate itself being insoluble in the phosphor. After subsequent addition of 10 ml of the phosphor the bottles were shaken and left in the dark for a few hours prior to counting to minimise phosphorescence.

The counting apparatus used (Panax type SC/L P2.) consisted of a single photo-multiplier tube optically coupled to the glass sample container by a bath of silicone oil, the whole arrangement being contained in a lead castle, and connected to a scaler and timer (Panax type STN.1).

The chromatogram of a sample of diphenylthallium bromide which had been precipitated and washed with ether during a kinetic run was compared with the chromatogram of a mixture of unreacted diphenylthallium bromide and diphenylmercury. The thin layer chromatogram<sup>4</sup> of the precipitated diphenylthallium bromide had only one spot whose  $R_f$  value compared favourably with that of unreacted diphenylthallium bromide.  $R_f$  value of unreacted  $\text{Ph}_2\text{TlBr}$  0.14, and  $\text{Ph}_2\text{Hg}$  0.84;  $R_f$  value of precipitated  $\text{Ph}_2\text{TlBr}$  0.15, no other spots.

For each kinetic run a total of 6 samples were taken, 5 were withdrawn serially within the first 7 h and the last after 24–30 h. From the measured count rate the fraction of exchange ( $F$ ) that had occurred in time  $t$  could be calculated:

$$F = \frac{S_t - S_0}{S_0 - S_\infty}$$

where  $S$  = specific activity and the subscript refers to time.

A plot of  $\ln(1 - F)$  vs. time yielded a straight line in every case indicating that a first order exchange process was occurring. The slope of  $\ln(1 - F)$  vs.  $t$  plot yielded the 1st order rate constant  $K$ .

The method of least squares was applied to each  $\ln(1 - F)$  vs.  $t$  plot in order to determine  $K$ . In all the runs conducted the spread of the points about the best straight line was not more than  $\pm 8\%$ .

The order of the reaction with respect to each of the components was deduced by determining the rate of the reaction  $R$  at various concentrations of that component

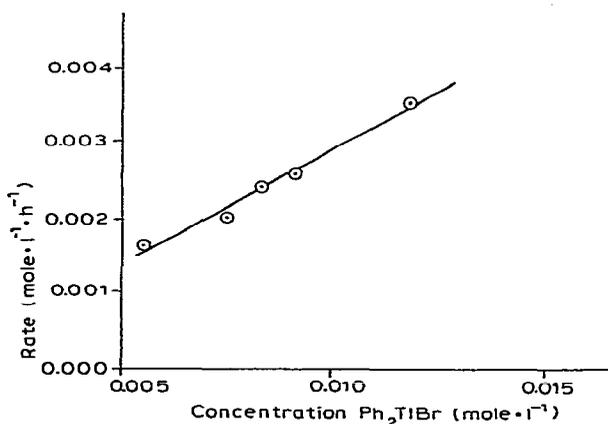


Fig. 1. Determination of order with respect to diphenylthallium bromide (temp.  $105^\circ$ , conc.  $\text{Ph}_2\text{Hg}$   $0.0938$   $\text{mole}\cdot\text{l}^{-1}$ ).

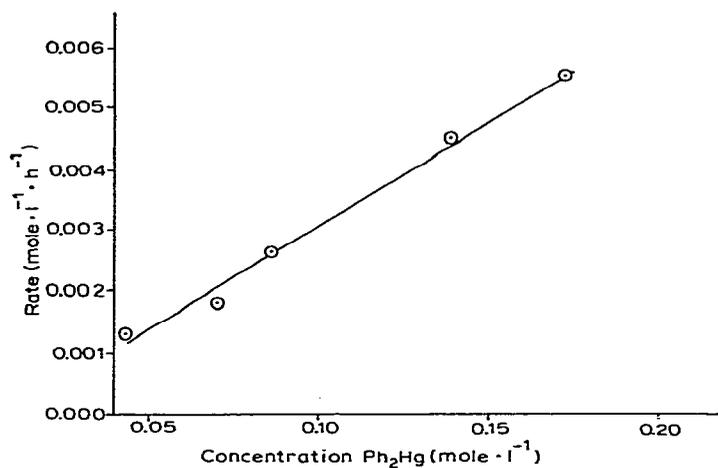


Fig. 2. Determination of order with respect to diphenylmercury (temp. 105°, conc. Ph<sub>2</sub>TlBr 0.0085 mole · l<sup>-1</sup>).

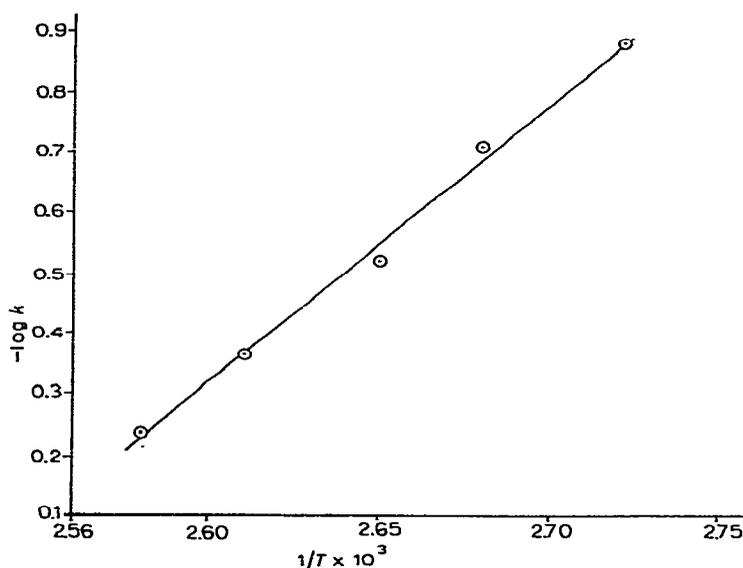


Fig. 3. Determination of activation energy (conc. Ph<sub>2</sub>Hg 0.092 mole · l<sup>-1</sup>; Ph<sub>2</sub>TlBr 0.0075 mole · l<sup>-1</sup>).

in the normal way. On the concentration *vs.* rate graphs the spread of values of *R* about the best straight line drawn through the points was  $\pm 3\%$  when varying diphenylthallium bromide and  $\pm 6\%$  when varying diphenylmercury.

The activation energy of the reaction was determined by measuring *K* at various temperatures, at constant component concentration, and plotting  $\ln K$  *vs.*  $1/T$  (Fig. 3).

Using the Arrhenius equation:  $\ln K = E_a/(R \cdot T) + c$ , the activation energy,  $E_a$  was deduced from the slope of the graph.

The value of  $K$  was measured at 5 different temperatures and all the points on the  $\ln K$  vs  $1/T$  plot fell within  $\pm 5\%$  of the best straight line.

The results of the order determination shown graphically in Figs. a and 2 indicate that the reaction is 1st order with respect to both diphenylthallium bromide and diphenylmercury.

The values of activation energy  $E_a$ , activation enthalpy  $\Delta H^*$ , free energy of activation  $\Delta F^*$  and entropy of activation  $\Delta S^*$  were deduced from the normal thermodynamic relationships and are given in Table 1.

TABLE 1

## ACTIVATION PARAMETERS

$E_a$	= 21.3 kcal · mole <sup>-1</sup>
$\log_{10} PZ$	= 9.25
$\Delta F^*$	= 27.6 kcal · mole <sup>-1</sup>
$\Delta H^*$	= 20.6 kcal · mole <sup>-1</sup>
$-\Delta S^*$	= 18.6 kcal · mole <sup>-1</sup>

## DISCUSSION

It can be shown that for a simple bimolecular reversible isotope exchange reaction the relation:

$$-\log_{10}(1-F) = \frac{R}{2.303} \cdot \left(\frac{a+b}{a \cdot b}\right) \cdot t \quad (1)$$

will be obeyed<sup>8</sup>. Here  $a$  is the concentration of active plus inactive diphenylthallium bromide, and  $b$  is the concentration of active plus inactive diphenylmercury. From the order determination it was found that the reaction is 1st order in each component and hence we can write:

$$R = K'' \cdot a \cdot b \quad (2)$$

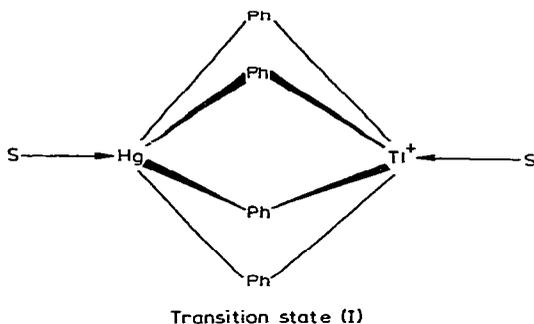
where  $K''$ , the overall 2nd order rate constant.

Substituting (2) in (1):

$$-\log_{10}(1-F) = \frac{K''}{2.303} \cdot (a+b) \cdot t$$

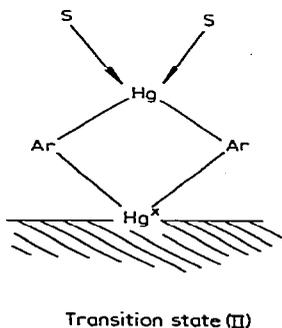
The graph of  $-\log_{10}(1-F)$  vs. time was a straight line in every case thus showing that the relationship (1) was obeyed.

The conditions employed of relatively non-ionising solvent and low temperature tend to preclude a mechanism proceeding by an ionic or a free radical process. Such ionic and radical mechanisms as have been proposed<sup>1</sup> have taken place in more forcing conditions than this study. As in other reports of reactions of diarylmercury compounds which we have studied<sup>4,9</sup> we propose that the reaction proceeds via a bimolecular transition state of the form:



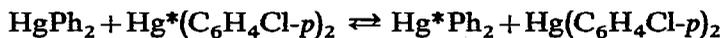
where S represents a solvent molecule. Both  $\text{Ph}_2\text{Hg}$  and  $\text{Ph}_2\text{Tl}^+$  are  $sp$  hybridized with two remaining unoccupied  $p$  orbitals. Thus an electron donor solvent could co-ordinate to form first an  $sp^2$  arrangement and then an  $sp^3$  arrangement depending on whether one or two molecules were co-ordinated. Such co-ordination would plainly enhance the formation of the above transition state.

An example of the effect of this co-ordination can be taken from work<sup>9</sup> carried out on the exchange, in various solvents, of mercury between diphenylmercury and metallic mercury. The transition state invoked in this work was similar to that proposed here, *viz.* :



Here the activation energy in benzene, a non-co-ordinating solvent, was  $18.5 \text{ kcal} \cdot \text{mole}^{-1}$  while in pyridine, a strongly co-ordinating solvent, it was  $11.2 \text{ kcal} \cdot \text{mole}^{-1}$  showing the effect of the electron donor solvent on the ease of formation of the transition state.

We have recently investigated the exchange of aryl groups between various diarylmercury compounds<sup>4</sup>. In that work the same type of bimolecular transition state was consistent with the proposed mechanism. In this case the fact that no mixed compounds (*e.g.*  $\text{Ar}'\text{-Hg-Ar}$ ) were formed indicated that the exchange proceeded via a unique transition state of this type. The reaction of diphenylmercury and di(*p*-chlorophenyl)mercury in pyridine was studied in detail:



and the activation parameters determined. The activation energy for the reaction was  $11.2 \text{ kcal} \cdot \text{mole}^{-1}$ .

The activation energy of a reaction proceeding via a transition state may be considered as a measure of the difficulty with which the transition state is formed. A comparison of the activation energy for the two reactions shows that the formation of the transition state here is more difficult than the formation of the corresponding state for the mercury exchange. This is interesting in view of the fact that  $\text{TlPh}_2^+$  and  $\text{HgPh}_2$  are isoelectronic. If the transition state is in fact as proposed then any extra stability of the linear arrangement of  $\text{Ph-Hg-Ph}$  or  $\text{Ph-Tl}^+-\text{Ph}$  would detract from its formation. It could be argued that the phenyl group's  $\pi$  electrons are delocalised over the metal atom in each case thus increasing the stability of the linear arrangement. This effect would be expected to be similar in each case. We must attribute the dramatic increase in  $E_a$  to the repulsive effect of the charge on the electrophile and smaller size of the Tl nucleus. Also the rate of the reaction of diphenylmercury with diphenylthallium was very much less than that of diphenylmercury and bis(*p*-chlorophenyl)mercury. This again can be attributed to the inhibiting effect on the electrophile of the positive charge, and that the metal to carbon bond in the diphenylthallium ion is stronger than that in bis(*p*-chlorophenyl)mercury and that the transition state, once formed, takes longer to decompose to products.

$\Delta S^*$  values are significantly lower than those reported for similar bimolecular transition states<sup>4,9</sup>. Further work is to include investigations into the effect of ring substituents on the reaction parameters, and solvent effects on the reaction. Though here difficulties occur due to the limited solubility of the thallium organometallic compounds. This work should help to explain the  $\Delta S^*$  values and enable us to confirm or reject the proposed transition state.

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