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EXCHANGE OF ORGANOMETALLIC COMPOUNDS WITH MERCURY METAL

VII *. INTERACTION OF DI-*p*-ANISYLTHALLIUM CHLORIDE WITH MERCURY IN PYRIDINE, ETHYLENEDIAMINE AND DIMETHYL SULFOXIDE; PREVAILING ROLE OF HOMOGENEOUS REACTION

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Summary

Kinetic study of the interaction of di-*p*-anisylthallium chloride with mercury metal, in pyridine, ethylenediamine, or dimethyl sulfoxide solutions, show that in the former two solvents with the following experimental conditions: solution volume 10 ml, mercury surface area 10 cm^2, 60°C, and without stirring of mercury, the Hg/Tl exchange occurs via the homogeneous reaction (80—90 percent) with dissolved mercury. In DMSO, under the same experimental conditions, the contribution of the homogeneous reaction is nearly the same as that of the heterogeneous one. This was determined by the study of the experimental exchange rate dependence on organic phase volume, and mercury or di-*p*-anisylthallium chloride solubilities in the solvents, as well as from analysis of kinetic curves for the exchange in saturated and unsaturated solutions of mercury metal in the solvents studied.

In the same reactor (polarographic cell) the Hg/Hg exchange of organomercurials with Hg metal may be thought to occur via a heterogeneous reaction as the prevalent process. The difference in behaviour between organothallium and organomercury compounds may be explained by the far lower adsorbance of organothallium compounds when compared with the respective organomercury compounds. The possible mechanism of the Hg/Tl exchange involving organobimetallic intermediates is proposed.

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* See ref. 1 for Part VI.

Introduction

In previous papers of this series [1,2] it was shown that diethyl- and diarylthallium chlorides, when adsorbed on a mercury surface from aqueous/methanol 9 : 1 solutions, gave a short-lived species for which the structure of the organobimetallic cation, $RHgTl^+R$ has been proposed. It was suggested that such species were responsible for occurrence of the redox Tl/Hg exchange between mercury metal and organic compounds of thallium(III), the reaction was discovered by Gilman and Jones [3] (eq. 1).

$$Ar_2Tl^+ + Hg \xrightarrow{Py} Ar_2Hg + Tl^+ \qquad (1)$$

Reaction 1, as well as the Hg/Hg exchange between Ar_2Hg or ArHgX and Hg metal [4—21], is considered to be a heterogeneous process on the mercury surface. With arylmercury compounds the homogeneous exchange occurring in benzene solutions of mercury metal was also studied and it has been shown [15], that its contribution to the overall exchange rate is negligibly small as compared with the heterogeneous reaction.

In this report we want to demonstrate that reaction 1, when carried out on an unstirred mercury surface, in pyridine or ethylenediamine, may occur mainly via a homogeneous process with the exchange rate depending on mercury metal concentrations in the organic solvents.

Results

Reaction of $(p\text{-}CH_3OC_6H_4)_2TlCl$ with mercury was studied in three solvents: pyridine, ethylenediamine, and dimethyl sulfoxide at 60°C. The kinetics were studied by polarographic techniques. As the reaction progresses the wave potential of TlCl increases, while the first wave of the electroreduction of di-*p*-anisylthallium chloride decreases, as measured by the polarograms of the reaction mixtures.

The polarographic half-wave potentials for TlCl and the first wave of $(p\text{-}CH_3OC_6H_4)_2TlCl$ in the three solvents studied are listed in Table 1.

The kinetic measurements were based on both the rate of decrease in the height of the first $(p\text{-}CH_3OC_6H_4)_2TlCl$ wave and the rate of increase in the TlCl wave height. Because the kinetic studies were carried out using polarographic techniques, Et_4NClO_4, (0.1 *M*) was added to all systems. All the reaction rates were measured in the same reactor (polarographic cell) under the unstirred mercury surface. The mercury pool area was 10 ± 0.5 cm². The solution volume over the mercury pool was 10 cm³, with exception of the runs in which the solution volume effect was to be studied. Concentrations of di-*p*-anisylthallium chloride were 1×10^{-4} to 6×10^{-4} *M*. The exchange reactions studied were, in most cases, very slow, therefore the rates could only be measured up to a small interconversion percentage (10—30%).

When a solution of $(p\text{-}CH_3OC_6H_4)_2TlCl$, heated to 60°C in pyridine or ethylenediamine is poured into the polarographic cell containing the mercury pool and kinetic measurements made, then strange S-shaped kinetic curves are observed, (Figs. 1 and 2, curves "a"). The kinetic curves show induction periods of

TABLE 1

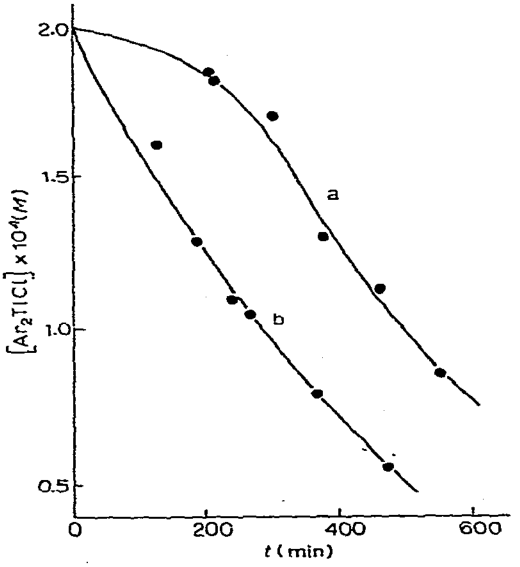
THE $E_{1/2}$ VALUES FOR TlCl AND THE FIRST WAVE OF $(p\text{-}CH_3OC_6H_4)_2TlCl$

Solvent	$-E_{1/2}$(TlCl) (V; SCE)	$-E_{1/2}$ [$(p\text{-}CH_3OC_6H_4)_2TlCl$]
Py	0.49	0.91
EDA	0.70	1.11
DMSO	0.56	0.96

200—300 min, followed by the morphologically "normal" parts of the curves.

When, however, the saturated solutions of mercury metal in pyridine or EDA were prepared by shaking the solvent with mercury for 3 h at 60°C, then the kinetic curves are "normal" from the beginning of the reaction; the curves correspond to second order kinetics (Figs. 1 and 2, curves "b").

This leads to an assumption that the induction periods, during which the reactions are very slow, are due to mercury dissolution kinetics. When the mercury content in solution is small, the reaction is slow, the accumulation of mercury in the solution results in a stationary mercury concentration and the interaction of the organothallium compound with mercury metal, instead of the mercury dissolution, becomes the rate-limiting step. The induction period depends on the volume of the reaction solution, the induction period increases with an increase in solution volume. This is, obviously, due to a slower achievement of the stationary concentration in solutions of large volume. (The mercury pool



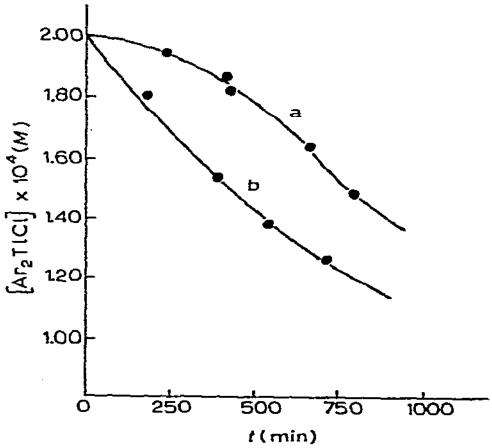


Fig. 1. Kinetic curves for the reaction of di-p-anisylthallium chloride with mercury in ethylenediamine at 60°C. Curve (a) for the reaction in pure solvent; curve (b) for the reaction in saturated solution of mercury metal in EDA. Concentration of $(p\text{-}CH_3OC_6H_4)_2TlCl$ 2×10^{-4} M; $S = 10$ cm^2; $V = 10$ ml, unstirred mercury.

Fig. 2. The same as in Fig. 1 for reaction in pyridine.

TABLE 2

THE APPARENT RATE CONSTANTS FOR Tl/Hg EXCHANGE OF DI-*p*-ANISYLTHALLIUM CHLORIDE WITH MERCURY METAL IN VARIOUS SOLVENTS PREVIOUSLY SATURATED BY MERCURY. THE MERCURY POOL AREA $S = 10$ cm^2; THE WORKING SOLUTION VOLUME 10 ml; 0.1 *M* Et_4NClO_4 AT 60°C

Solvent	Concentration of Ar_2TlCl $\times 10^4$ (*M*)	$k_1^* \times 10^6$ (sec^{-1})	Solubility of mercury metal [a] at 60°C (g-atom. l^{-1})	Solubility of Ar_2TlCl at 60°C (M^{-1})
Pyridine	1	9.2 ± 0.8	2.5×10^{-5}	0.09
	2	10.5 ± 1.1		
	4	8.4 ± 0.7		
	6	6.6 ± 0.6		
Ethylenediamine	2	50 ± 3	1.6×10^{-4}	0.48
Dimethyl sulfoxide	2	(1.0)	(4×10^{-6})	0.22
Dimethyl formamide	2	14.7 ± 2 [b]	5×10^{-5}	0.02

[a] See text; [b] Ref. 22.

area was the same in all runs.) Thus, the Tl/Hg exchange occurs mainly via a homogeneous reaction. The reaction in DMSO is very slow ($t_{1/2}$ ca. 21 days) which make kinetic studies rather difficult; the reaction was carried out only up to ca. 10% conversion (for 35 h at 60°C), the induction period in the reaction was imperceptible.

Results of the kinetic studies are given in Table 2. In this Table, k_1^* is the apparent first order rate constant which defines the rate of disappearance of $(p\text{-}CH_3OC_6H_4)_2TlCl$ or the rate of accumulation of TlCl in solution. It follows from Table 2 that the k_1^* value depends on the organothallium compound concentrations, it increases by a factor of 1.5 with a 6-fold increase in the concentration. Log c_0/c vs. t (min) values are plotted in Fig. 3. The apparent exchange rate also depends on the organic phase volume (Table 3; Fig. 4). The

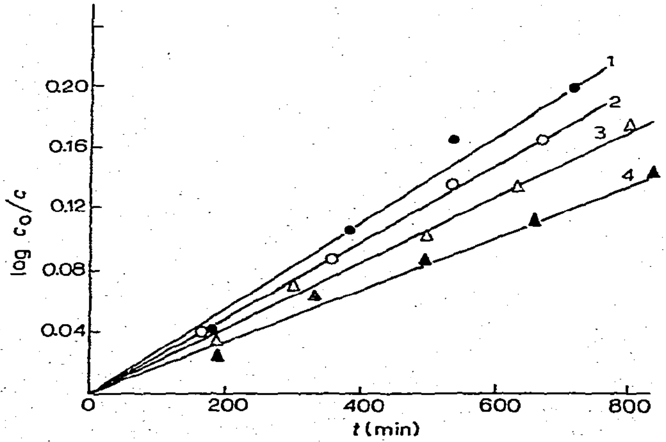


Fig. 3. Logarithmic plots of the kinetic curves for Tl/Hg exchange in pyridine at 60°C. Concentrations of $(p\text{-}CH_3OC_6H_4)_2TlCl$: 1×10^{-4} *M* (1); 2×10^{-4} *M* (2); 4×10^{-4} *M* (3); 6×10^{-4} *M* (4); $S = 10$ cm^2; $V = 10$ ml, unstirred mercury.

TABLE 3

EFFECT OF VOLUME (V) OF THE SOLUTION OF $(p\text{-}CH_3OC_6H_4)_2TlCl$ (2×10^{-4} M) ON THE Tl/Hg EXCHANGE RATE IN EDA OR PYRIDINE SATURATED BY MERCURY METAL AT 60°C. THE MERCURY POOL AREA, $S = 10$ cm^2; 0.1 M Et_4NClO_4

V (ml)	$k_1^* \times 10^6$ in EDA (sec^{-1})	$k_1^* \times 10^6$ in Py (sec^{-1})
5	54 ± 3	13 ± 1
5	54 ± 3	14 ± 1
10	50 ± 3	10.5 ± 1
25	47 ± 3	9.8 ± 1

rate constant decreases with the solution volume; which should occur for heterogeneous reactions.

Thus, the data obtained show that the Tl/Hg exchange has complex kinetics, the exchange proceeds, obviously, via both homogeneous and heterogeneous paths, simultaneously.

Discussion

Considering the exchange which occurs simultaneously via homogeneous and heterogeneous mechanisms, one can write the following expression for the overall reaction rate (eq. 2). The apparent first-order rate constant, k_1^*, which

$$\text{rate} = k_{\text{hom}}[Ar_2TlCl][Hg] + k_{\text{het}}^*[R_2TlCl] \qquad (2)$$

is an experimental characteristic of the rate of disappearance of R_2TlCl or

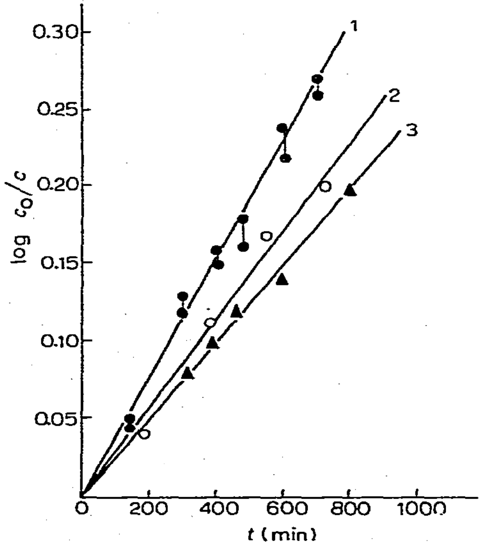


Fig. 4. Logarithmic plots of the kinetic curves for Tl/Hg exchange in pyridine at 60°C. Concentration of $(p\text{-}CH_3OC_6H_4)_2TlCl$ 2×10^{-4} M. Volumes of working solution: 5 ml (1); 10 ml (2); 25 ml (3). $S = 10$ cm^2; unstirred mercury.

accumulation of TlCl in solution, is given by eq. 3, where k_{hom} is the second

$$k_1^* = k_{\mathrm{hom}}[\mathrm{Hg}]_s + k_{\mathrm{het}}^* \tag{3}$$

order rate constant of the homogeneous reaction of R_2TlCl with dissolved mercury metal, k_{het}^* (sec^{-1}) is the "observed" rate constant of the heterogeneous reaction which is measured as the rate of dissappearance of R_2TlCl or accumulation of TlCl in solution owing to the Tl/Hg exchange on the given mercury surface area (10 cm^2), $[\mathrm{Hg}]_s$ is the concentration of the soluted mercury, and $[Ar_2TlCl]$ is the concentration of di-*p*-anisylthallium chloride in solution.

The number of moles (n) of Ar_2TlCl which are transferred over all the mercury surface area (S) per second is given by eq. 4, where k_{het} ($\mathrm{mol}(10\ \mathrm{cm}^2)\ \mathrm{sec}^{-1}$)

$$n = k_{\mathrm{het}}[Ar_2TlCl]\theta \tag{4}$$

is the "true" rate constant of the heterogeneous exchange, θ is a coverage of the mercury surface, $[Ar_2TlCl]$ is a concentration of Ar_2TlCl in solution *. The overall amount of Ar_2TlCl in solution, where V is the solution volume, is given

$$N = [Ar_2TlCl]\ .V \tag{5}$$

by eq. 5. Eq. 7 is obtained from eqs. 4 and 5 (eq. 6), with substitution in eq. 3.

$$k_{\mathrm{het}}^* = \frac{n}{N} = \frac{k_{\mathrm{het}} \cdot \theta}{V} \tag{6}$$

$$k_1^* = k_{\mathrm{hom}}[\mathrm{Hg}]_s + \frac{k_{\mathrm{het}} \cdot \theta}{V} \tag{7}$$

Eq. 7 connects the "observed" rate constant for disappearance of Ar_2TlCl (or accumulation of TlCl) with the true homogeneous and heterogeneous constants. From eq. 7 the plot of k_1^* vs. $1/V$ must be a straight line with intercept $k_{\mathrm{hom}}[\mathrm{Hg}]_s$ and slope $k_{\mathrm{het}}\theta$.

Fig. 5 shows the k_1^* vs. $1/V$ plots for pyridine and ethylenediamine solutions. The k_{hom} values were calculated from the intercepts, $k_{\mathrm{hom}}[\mathrm{Hg}]_s$, of these plots. For the calculations the $[\mathrm{Hg}]_s$ values must be known, i.e. mercury concentrations in the saturated pyridine and ethylenediamine solvents. The mercury solubilities in the two solvents as well as in DMSO and DMF were measured as follows. The solvent was shaken with excess of mercury metal for 3 h at 60°C and then $(p\text{-}CH_3OC_6H_4)_2$-TlCl was dissolved in concentration 1×10^{-4} to 4×10^{-4} *M*. This solution was kept for 2—3 days at 60°C till all the organothallium compound had undergone the Tl/Hg exchange. Then the remaining concentration of $(p\text{-}CH_3OC_6H_4)_2TlCl$ was measured by polarographic techniques and the amount of organothallium compound which had reacted with mercury solution was calculated as the difference between *c*(initial) and *c*(rem.). The *c*(initial) — *c*(rem.) value is equal to the mercury concentration in the saturated solution. Solubilities of mercury metal in various solvents at 60°C are given in Table 2.

Kinetics of the second order homogeneous reaction were studied with the saturated mercury solutions in each solvent. The experimental data for pyridine

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* i.e. it is suggested that the Henry isotherm is valid.

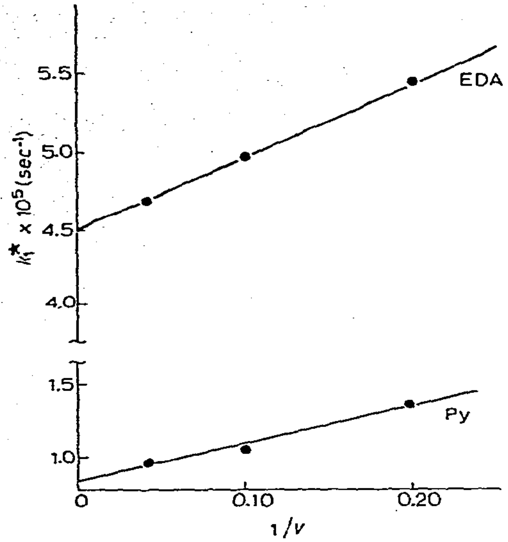


Fig. 5. k_1^* vs. $1/V$ plots for Tl/Hg exchange of $(p\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{TlCl}$ in pyridine and EDA at 60°C. $c_0 = 2 \times 10^{-4}$ M; $S = 10$ cm^2; unstirred mercury.

and EDA solutions are given in Table 4. k_{hom}(DMSO) was not determined because of the poor solubility of mercury in DMSO.

The last column of Table 4 shows that k_{hom} values calculated using eq. 7 from the k_1^* vs. $1/V$ plots drawn in Fig. 5. k_1^* increases as the volume decreases, this is due to the second term of eq. 7; at large volumes the homogeneous reaction in which the rate is independent of the volume dominates, at small volumes however, the heterogeneous reaction makes the main contribution. From Fig. 5 one can calculate that the heterogeneous reaction contribution to the overall exchange rate is ca. 16% for 10 ml of pyridine solution. In EDA the corresponding value is 10%. One can also predict that the contributions of the homogeneous and heterogeneous reactions will be nearly the same when the thickness of the layer of solution covering the mercury surface area of 10 cm^2 is about 1 mm for pyridine and EDA solutions. Thus, in our reactor ($S = 10$ cm^2, $V = 10$ ml,

TABLE 4

RATE CONSTANTS (k_{hom}, l mol^{-1} sec^{-1}) OF THE HOMOGENEOUS REACTION BETWEEN DI-p-ANISYLTHALLIUM CHLORIDE AND SOLUTIONS OF MERCURY METAL AT 60°C

Solvent	$[\text{Ar}_2\text{TlCl}] \times 10^4$ (M)	k_{hom} experimental	k_{hom} calculated [a]
Pyridine	1.0	0.09	
	2.0	0.07	0.36
EDA	2.0	0.17	
	2.0	0.07	
	2.0	0.14	
	4.0	0.13	0.28

[a] Calculated from Fig. 5 and eq. 7.

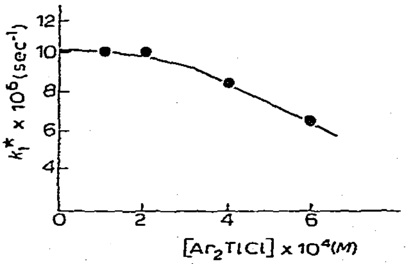
unstirred mercury) di-*p*-anisylthallium chloride undergoes Tl/Hg exchange mainly via a homogeneous reaction.

The slower exchange rate at larger volumes may also be due to slower mercury dissolution: in large solution volume, without stirring, mercury concentration does not achieve that corresponding to a saturated solution. The plot in Fig. 6 shows that at higher $(p\text{-}CH_3OC_6H_4)_2TlCl$ concentrations k_1^* becomes much smaller. A possible explanation is that dissolved mercury reacts faster than the concentration supplied by gradual dissolution of the mercury pool. However at, and below 2×10^{-4} *M* concentration the reaction rate is independent of $[(p\text{-}CH_3OC_6H_4)_2TlCl]$ (Fig. 6), and because most of our measurements were carried out in 1 to 2×10^{-4} *M* $(p\text{-}CH_3OC_6H_4)_2TlCl$ solutions the concentration effect may be neglected.

In DMSO reaction 1 is very slow and it is difficult for accurate measurements of k_1^* and k_{hom} to be made. One may only make a qualitative estimation of the homogeneous and heterogeneous contributions in DMSO. The estimation gives ca 60% contribution of heterogeneous reaction at $V = 10$ ml in DMSO, and a k_{hom} value of 0.08 M^{-1} sec^{-1}, from eq. 7. Thus, unlike EDA and pyridine, reaction 1 in our reactor is mainly heterogeneous in DMSO.

If the exchange was a purely heterogeneous process, the reaction would be very slow (with k_1^* of about 10^{-6} sec^{-1}). This is understandable because the heterogeneous reaction occurs in a monolayer of organothallium molecules adsorbed on the interface. Diarylthallium chlorides adsorb on the mercury surface rather poorly, even from aqueous solutions [24], and adsorption from organic solvents would be even less. Therefore the surface coverage, θ, should be small and the heteregeneous exchange rate will be slow.

The homogeneous reaction contribution will be as high as the mercury solubility in a given solvent. It follows from the plot in Fig. 7 that the overall exchange rates show a linear dependence on mercury solubilities; the slope is



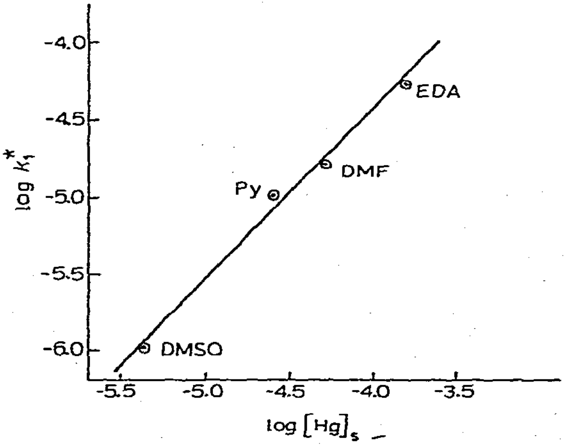


Fig. 6. k_1^* vs. $[(p\text{-}CH_3OC_6H_4)_2TlCl]$ plot for Tl/Hg exchange at 60°C. $S = 10$ cm^2; $V = 10$ ml; unstirred mercury.

Fig. 7. Log k_1^* vs. log $[Hg]_S$ plot for four solvents: $c_0 = 2 \times 10^{-4}$ *M*; $S = 10$ cm^2; $V = 10$ ml; unstirred mercury.

nearly unity. The linear log k_1^* vs. log $[\mathrm{Hg}]_s$ dependence indicates that k_{hom} is practically independent of the nature of the amine solvent. If the rate of the heterogeneous reaction is neglected, one can see from eq. 7 that log $k_1^* =$ log k_{hom} — log $[\mathrm{Hg}]_s$, where $[\mathrm{Hg}]_s$ is the mercury solubility, and from the plot in Fig. 7, the average homogeneous reaction rate may be calculated, (0.25 M^{-1} sec^{-1} with $1/V = 0$; cf. the data in Table 4).

The negligible solvent effect on the exchange rate indicates that there is no addition solvation or desolvation of reagents in the transition state, i.e., the exchange probably has a reagent-like transition state.

Eq. 7 allows us to calculate the $k_{\mathrm{het}}\theta$ values from the k_1^* vs. $1/V$ slopes. These values are 5×10^{-5} cm^3 sec^{-1} for EDA and 2×10^{-5} cm^3 sec^{-1} for pyridine. If θ is 1% than k_{het} is ca. 10^{-1} cm^3 sec^{-1} for $S = 10$ cm^2.

We now compare the Tl/Hg exchange with the data for Hg/Hg exchange in organomercury compounds (eq. 8).

$$\begin{array}{l} \mathrm{R_2Hg + Hg^* \rightarrow R_2Hg^* + Hg} \\ \mathrm{RHgX + Hg^* \rightarrow RHg^*X + Hg} \end{array} \qquad (8)$$

There are three main diagnotic tests which enable us to determine the preferable reaction path; a homogeneous or heterogeneous one. The tests are studies of exchange rate dependence on (i) solution volume, (ii) organometallic solubilities and (iii) mercury solubility in a given solvent. Table 5 contains the comparison between organomercury and organothallium compounds. The available data do not allow us to determine whether the rate of reaction 8 is dependent on the solution volume. The Hg/Hg exchange was carried out with extensive stirring of the mercury pool [11]; the stirring results in dispersion of mercury metal to small droplets separated by a solvent film. The droplets were rather stable and did not merge into one large drop for several hours [11]. The 75 g mercury sample had 899 cm^2 surface area under these conditions [11], therefore the thickness of the layer of the solution covering the mercury surface changed little with the solution volume and an accurate estimation of k_1^* vs. $1/V$ dependence cannot be made if based on this experimental data. However, the solubility effects are the opposite for organomercurials when compared to the organo-

TABLE 5

COMPARISON OF EXPERIMENTAL DATA ON Tl/Hg AND Hg/Hg EXCHANGES OF ARYL COMPOUNDS

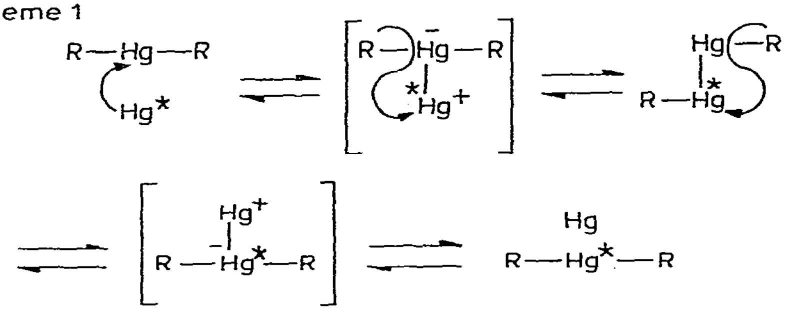
Effect on k_1^*	$\mathrm{PhHgBr(Cl)}$ or $\mathrm{Ph_2Hg}$ (Refs)	$(n\text{-}\mathrm{CH_3OC_6H_4})_2\mathrm{TlCl}$ (this work)
(i) of solution volume	poorly expressed [12]; see text	k_1^* decreases with increase in volume
(ii) of organometallic compound solubility in a given solvent	k_1^* decreases with increase in solubility	no dependence
(iii) of solubility of mercury metal in a given solvent	no dependence	k_1^* increases with $[\mathrm{Hg}]_s$

thallium compound (Table 5). The Hg/Hg exchange rate decreases with the solubility of ArHgX(Ar_2Hg) and is independent of mercury solubility in various solvents studied (HMPT, benzene, toluene, methanol, water, isooctane, nitrobenzene; see ref. 23 for a review). In contrast, the Tl/Hg exchange rate increases with mercury solubility (Fig. 7), but is independent of Ar_2TlX solubilities.

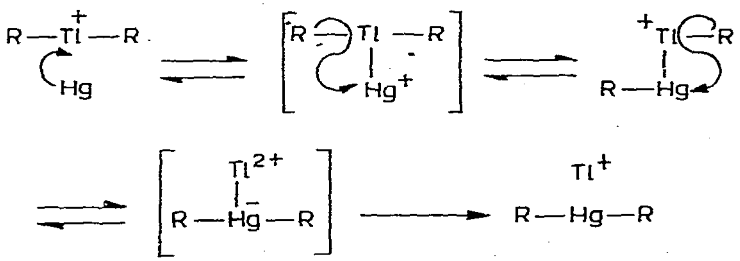
Thus from Table 5 it may be concluded that the organomercury exchange is, in the main, a heterogeneous process when the mercury pool is stirred [15]. Therefore, one may expect that the adsorption of an organomercury compound will be lower the greater its solubility. This should result in a decrease of the $k_{het}\theta$ value and retardation of the heterogeneous exchange rate. However, in our experiments with di-*p*-anisylthallium chloride such effects did not occur (Tables 2 and 5). The Tl/Hg exchange with the unstirred mercury pool has obviously a low $k_{het}\theta$ value. In this connection organothallium compounds have a poorer adsorbance on mercury as compared with organomercurials [24].

Both the Hg/Hg and Tl/Hg exchanges probably have a common mechanism which involves organobimetallic compounds, with metal—metal bonds, as intermediates [23]. For organomercury and organothallium compounds the proposed mechanisms are shown in Schemes 1 and 2 respectively.

Scheme 1



Scheme 2



Experimental

Materials

Tetraethylammonium perchlorate was prepared from tetraethylammonium iodide (Reanal; pure grade) and an equimolar amount of $Mg(ClO_4)_2$ (pure grade) in methanol. The product was recrystallised twice from methanol and dried under P_2O_5 in vacuo. Dimethylsulfoxide (commercial, pure grade) was shaken with BaO for two days and was then filtered and distilled under CaH_2 in a current of dry argon in vacuo; b.p. 32°C/1 mmHg. Ethylenediamine (commercial, 70% content) was dried with fused KOH, distilled under a fresh portion of KOH and then twice under sodium in a current of dry argon. The purified ethylenediamine gave a blue solution with sodium. Pyridine (pure grade) was purified via pyridinium perchlorate as described in ref. 25. Di-*p*-anisylthallium chloride was prepared as described in refs. 2 and 22.

Kinetic measurements

These were all carried out in one standard polarographic cell at 60 ± 0.2°C. 5 to 25 ml of 0.1 *M* Et_4NClO_4 solution in the solvent to be studied was placed in the cell which contained 8.2 ml of mercury metal (10 ± 0.5 cm^2 mercury surface area), oxygen was then removed by bubbling dry pure argon through the solution. The respective amount of 2×10^{-2} *M* di-*p*-anisylthallium chloride solution in pure solvent was added so that the resulting Ar_2TlCl solution had a 1×10^{-4} to 6×10^{-4} *M* concentration. When the reaction had to be studied in mercury saturated solvents the solvent was previously shaken with excess of mercury for 3 h at 60°C and then all manipulations were made as above. Changes in analytical concentrations of TlCl and $(p\text{-}CH_3OC_6H_4)_2TlCl$ were traced during the reaction time, using polarographic techniques (capillary; 1.03 mg sec^{-1}; *t* 1.68 sec). The overall rate constants were calculated with help of the commonly used differential equations for first order kinetics. The reactions were carried out in 10 to 70% conversion at a given reaction rate.

For k_{hom} measurements, the saturated solutions of mercury metal in 50 ml of solvents, containing 0.1 *M* Et_4NClO_4 were prepared and studied at 60°C. The necessary amount of $(p\text{-}CH_3OC_6H_5)_2TlCl$ was added for the organothallium compound concentration to be 1×10^{-4} to 4×10^{-4} *M*. The 7 ml aliquotes of the reaction mixture were taken out at certain time intervals and TlCl concentrations were measured polarographically. The last aliquotes were taken out two days after the start of the reaction. The last polarograms showed the concentration of mercury which had reacted with the organothallium compound. This concentration was taken as an initial mercury concentration; it was used for calculations of the rate constants with use of the second order kinetic equation.

The solubility of di-*p*-anisylthallium chloride in various solvents was measured polarographically at 60°C using the Ilkovich equation. The solubility of mercury in various solvents was estimated as follows: 3 or 4 ml of mercury were shaken with 25 ml of 0.1 *M* Et_4NClO_4 solution in a given solvent for 5 h at 60°C. Then 10 ml of the resulting solution were placed in a polarographic cell, heated to 60°C and, after removal of oxygen, di-*p*-anisylthallium chloride was added until the concentration was 4×10^{-4} *M*. Polarograms of the starting solution were recorded quickly. Then this solution was poured into a test-tube and was kept at 60 ± 0.2°C for 2 or 4 days until all the mercury dissolved had reacted with the organothallium compound. The remaining organothallium compound was measured polarographically, which then allowed an estimate of the mercury solubility in a given solvent.

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