Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

RADICAL EXCHANGE REACTIONS BETWEEN ORGANOMERCURY COMPOUNDS

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(Received January 20th, 1970)

SUMMARY

Reactions of diphenylmercury with R'_2Hg (where $R'=CN, CCl_3, C\equiv CPh$) in dimethylformamide were studied by a polarographic method and have been found to yield $PhHgR'$, obeying the second-order kinetics. Addition of iodide displays negligible effect on the reaction rates. When $R'=CFClCOOEt, CF_2COOEt, CH_2COOCH_3, CH_2C_6H_5$, the reaction of Ph_2Hg with R'_2Hg does not occur. *p*-OCH_3 groups in Ph_2Hg increase the reaction rates. The results obtained are discussed in terms of the S_E2 mechanism.

Study of the radical exchange reactions (eqn. 1) in the series of organomercury compounds played an important role in elucidating the dependencies of electrophilic

$$R^1HgR^2+R^3HgR^4 \rightleftarrows R^4HgR^3+R^2HgR^4 \quad (1)$$
$$(\text{or } R^1HgR^4+R^2HgR^3)$$

substitution mechanism at a saturated carbon atom[1]. In general, their kinetics has been investigated by the labelled-atom technique employing radioactive ^{203}Hg isotope, and only recent works refer to the application of NMR spectroscopy.

In a convenient classification of Ingold[2,3] reactions (1) were divided into mono- di- and trialkyl type exchange reactions:

$$RHgX+Hg{*}X_2 \rightleftarrows RHg{*}X+HgX_2 \quad \text{(mono-)}$$
$$RHg{*}X+R'HgX \rightleftarrows RHgX+R'Hg{*}X \quad \text{(di-)}$$
$$R_2Hg+RHg{*}X \rightleftarrows RHgX+R_2Hg{*} \quad \text{(tri-)}$$
$$(X = \text{acid anion})$$

The dialkyl exchange may also involve[1] disproportionation and redistribution of the organomercury compounds:

$$RHgX+RHgX \rightleftarrows R_2Hg+HgX_2$$
$$R_2Hg+HgX_2 \rightleftarrows 2RHgX$$

Ingold's classification can be supplemented with another type of radical exchange observed between two symmetric organomercury compounds:

$$R_2Hg+R'_2Hg \rightleftarrows 2RHgR' \quad (2)$$

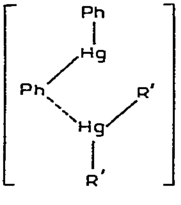
which analogously may be regarded as tetraalkyl exchange. Reactions of the last type were studied very little for the difficulties arising in determining the composition of the reaction mixture. It was found that an isotope equilibrium between mercurybisacetaldehyde and diphenyl- or di-*p*-anisylmercury installs almost instantaneously at 20° in acetone. However, the reaction does not take place with bis(*p*-chlorophenyl)mercury. The system $(C_6H_5)_2Hg/(p\text{-}ClC_6H_4)_2Hg$/pyridine also provided exchange of labelled mercury at 60°. With NMR technique the system $(C_6H_5)_2Hg/(CH_3)_2Hg$ was found to attain its complete equilibrium at 150° during 6 h. The exchange was studied also in systems: $(C_6Cl_5)_2Hg/Ph_2Hg$[6], $Me_2Hg/(C_6F_5)_2Hg$[7], and $Me_2Hg/PhC_2B_{10}H_{10}Hg$[8]. Probably the above reaction occurs via an intermediate unsymmetric organomercury compound RHgR′. In case of alkylmercury derivatives it was confirmed by the reaction of $(CH_3)_2Hg$ with $(CD_3)_2Hg$ which gave CH_3HgCD_3[9].

The present work is confined to the polarographic study of exchange reactions in the series of symmetric compounds (eqn. 2). This permitted to identify all the three compounds (R_2Hg, R'_2Hg and $RHgR'$) present in the reaction mixture. At the appropriate reaction rates this method allows to establish not the position of equilibrium alone but also to estimate the reaction rate constants for both forward (k_1) and back (k_{-1}) reactions:

$$R_2Hg + R'_2Hg \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2RHgR' \qquad K = \frac{[RHgR']^2}{[R_2Hg]\cdot[R'_2Hg]} \tag{3}$$

Study of the disproportionation reactions (3) was conducted for compounds R_2Hg where the radicals R occupy substantially different positions in the Kharasch order[10,11]. Diphenylmercury was employed as one reaction component whereas the other was R'_2Hg (where R′ is an electron-withdrawing group: $C{\equiv}CPh$, CCl_3, CH_2COOCH_3, $CHFCOOC_2H_5$, $CF_2COOC_2H_5$, $CClFCOOC_2H_5$ and CN). Reaction of diphenylmercury and HgI_2 was also studied for comparison.

We assumed that these reactions occur owing to the mercury atom in R'_2Hg compound attacking a carbon atom of the most nucleophilic Ph_2Hg★:



(I)

Different order of the nucleophilic character of Ph and R′ should result in the shift of equilibrium (3) towards the formation of PhHgR′, and k_1 is higher at the larger difference.

★ The transition state can also be a four-centered one (coordination of R′ with mercury of Ph_2Hg) but this is not of principal importance for the later analysis.

Kinetic study of the reactions was conducted directly in a polarographic cell in anhydrous dimethylformamide, in the presence of 0.1 *M* $(C_4H_9)_4NClO_4$ at 25 ± 0.2°. The reagent concentration varied within (1 to 4) · 10^{-4} mole/l. Constants were determined with an accuracy of no more than ±20%.

For the compounds $Hg(CH_2C_6H_5)_2$, $Hg(CH_2COOCH_3)_2$, $Hg(CF_2COOC_2H_5)_2$, and $Hg(FClCOOEt)_2$ an exchange with Ph_2Hg was not observed during several days. But in case of the last compound the polarographic waves of the starting components diminished at 25° in 24 h, and there appeared a prewave, corresponding probably to PhHgCFClCOOEt. Other R'_2Hg (R = CN, CCl_3, C≡CPh) compounds on reacting with Ph_2Hg shifted the equilibria almost entirely to PhHgR′.

At the reagent ratio of 1/1 after a certain period there were absolutely no polarographic waves of R'_2Hg and Ph_2Hg. But at the intermediate potentials there appeared a wave which in independent experiments has been found to be due to PhHgR′ and according to eqn. (3) had the height associated with the formation of the compound in a concentration twice that of each reagent (Fig. 1). Furthermore, polarographic study showed that compounds PhHgC≡CPh, PhHgCN and $PhHgCCl_3$ did not change in DMF at 25° in the presence of Bu_4NClO_4 after several days, which was also an evidence of the absence of reverse reaction ($k_1 \gg k_{-1}$). In all the cases the reaction obeyed the second-order kinetics. The rate constants are listed in Table 1.

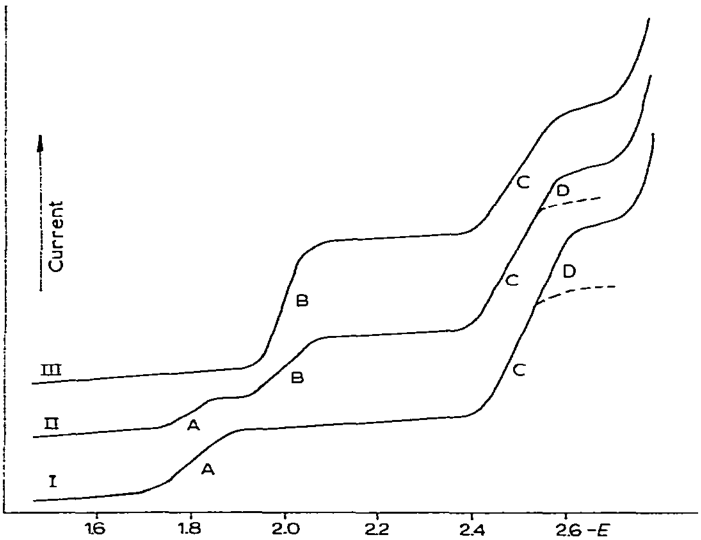


Fig. 1. Polarograms of the mixture Ph_2Hg (2 · 10^{-4} *M*)/$(PhC{\equiv}C)_2Hg$ (2 · 10^{-4} *M*) in DMF in the presence of 0.1 *M* Bu_4NClO_4. I, at the beginning of reaction; II, in the middle of reaction; III, at the end of reaction. Waves of: A = $(PhC{\equiv}C)_2Hg$; B = PhC≡CHgPh; C = PhC≡CH; D = Ph_2Hg.

The reactions were conducted at no less than 70% conversion. Anamorphoses of kinetic curves $(I_{d_0}/I_d - 1) - \tau$ are shown in Fig. 2, where I_{d_0} and I_d are the limiting diffusion currents corresponding to the starting and given concentrations of R′Hg (or Ph_2Hg) respectively, τ is the time.

Rate dependence upon the change of starting concentration of Ph_2Hg and

TABLE 1

RATE CONSTANTS OF THE REACTION BETWEEN Ph_2Hg AND R'_2Hg
DMF, 0.1 *M* Bu_4NClO_4, 25°.

R′	$k(l \cdot mole^{-1} \cdot sec^{-1})$
C≡CPh	0.30
CCl_3	0.61
CN	0.89

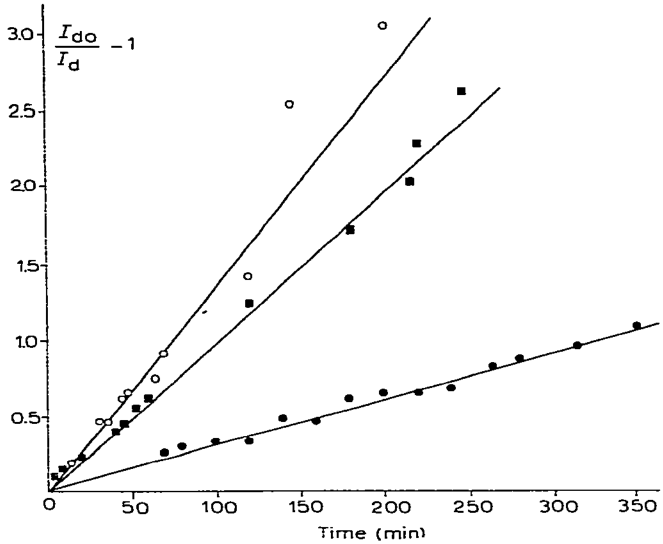


Fig. 2. Anamorphoses of kinetic curves of reaction $Ph_2Hg + R'_2Hg$ (0.1 *M* Bu_4NClO_4, DMF, 25°); ● PhC≡C, 0.193 m$M \cdot l^{-1}$; ■ CN, 0.198 m$M \cdot l^{-1}$; ○, CCl_3, 0.360 m$M \cdot l^{-1}$.

R'_2Hg was investigated for $(PhC{\equiv}C)_2Hg$ as an example. Within accuracy of the method the reaction rate constants obtained at the variation of both reagent concentrations coincide well (Table 2).

TABLE 2

RATE CONSTANTS OF THE REACTION $Ph_2Hg + (PhC{\equiv}C)_2Hg$
DMF, 0.1 *M* Bu_4NClO_4, 25°.

$[Ph_2Hg]_0 \cdot 10^3$(mole/l)	$[(PhC{\equiv}C)_2Hg]_0 \cdot 10^3$(mole/l)	$k\ (l \cdot mole^{-1} \cdot sec^{-1})$
0.193	0.193	0.29
0.372	0.372	0.27
0.378	0.191	0.32
0.192	0.384	0.31
		k_{mean} 0.30

Thus the data obtained provide the following order for the ability of compounds to exchange with diphenylmercury:

$$Hg(CN)_2 > Hg(CCl_3)_2 > Hg(C{\equiv}CPh)_2 > Hg(CClFCOOEt)_2 > Hg(CF_2COOEt)_2,\ Hg(CH_2COOCH_3)_2,\ Hg(CH_2C_6H_5)_2$$

As follows from this series the rate of formation of PhHgR′ shows a tendency to increase with enhancing difference in the order of nucleophilic character of the radicals.

To elucidate the effect of nucleophilic catalysis in the exchange reactions between Ph_2Hg and R'_2Hg the rates of the above reactions were determined in the presence of tetra-n-butylammonium iodide. Reaction of $(PhC{\equiv}C)_2Hg$ with Ph_2Hg was studied in dimethylformamide varying the concentration of Bu_4NI at the constant ionic strength of solution ($\mu = 0.1$) maintained by an addition of tetrabutylammonium perchlorate. The reaction rate of $(PhC{\equiv}C)_2Hg$ with Ph_2Hg increases (although negligibly) in the presence of iodide: even at 0.1 *M* concentration of Bu_4NI (500-fold excess in respect to the reagent concentrations) the reaction rate increases only 1.6-fold. The reaction retains its overall second order in the presence of iodide ions. As seen from the data of Table 3 at the varying starting concentrations the rate constants indicate the second-order reaction. The anamorphoses of kinetic curves are shown in Fig. 3. In the presence of iodide the reaction rate of $Hg(CN)_2$ with Ph_2Hg (k 0.14 l·mole^{-1}·sec^{-1}) decreases considerably. But the total second order

TABLE 3

RATE CONSTANTS OF THE REACTION OF Ph_2Hg WITH $(PhC{\equiv}C)_2Hg$
DMF, 0.1 *M* Bu_4NI, 25°

$[Ph_2Hg]_0 \cdot 10^3$ (mole/l)	$[(PhC{\equiv}C)_2Hg]_0 \cdot 10^3$ (mole/l)	k (l·mole^{-1}·sec^{-1})
0.198	0.098	0.49
0.146	0.146	0.51
0.193	0.193	0.53
0.286	0.286	0.52
0.370	0.370	0.49

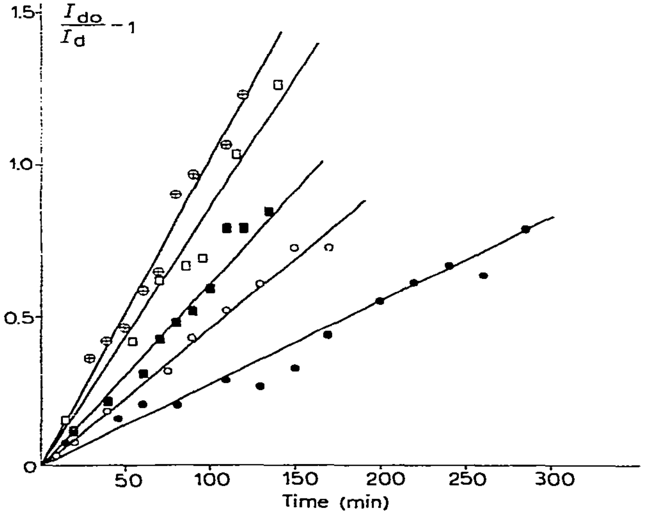


Fig. 3. Anamorphoses of kinetic curves of reaction $Ph_2Hg + (PhC{\equiv}C)_2Hg$ (0.1 *M* Bu_4NI, DMF, 25°); concentration: ●, 0.098; ○, 0.146; ■, 0.191; □, 0.286; ⊕, 0.370 m*M*·l^{-1}.

TABLE 4

REACTION RATES OF $Hg(CN)_2$ WITH Ph_2Hg
DMF, 0.1 *M* Bu_4NI, 25°

$[Ph_2Hg]_0 \cdot 10^4$ (mole/l)	$[Hg(CN)_2]_0 \cdot 10^4$ (mole/l)	k ($l \cdot mole^{-1} \cdot sec^{-1}$)
5.95	5.95	0.15
3.0	6.0	0.12
5.8	2.9	0.15

of reaction and the first order in each component are always maintained (Table 4).

Unfortunately, it is not possible to study the effect of iodide ion additives to the reaction of diphenylmercury with bis(trichloromethyl)mercury owing to decomposition of the latter to dihalocarbene[12]. However, judging from the change of the reaction rate constant at the starting part of the curve, the effect of iodide ion is insignificant.

Presence of iodide ions in the system $(PhCH_2)_2Hg/Ph_2Hg$ does not change the height of diphenylmercury wave. However, the wave of dibenzylmercury diminishes with time giving rise to a prewave. The latter probably appears due to an oxidation product of dibenzylmercury with traces of oxygen dissolved in DMF. In our opinion, such oxidation may be catalyzed by an iodide ion.

Besides investigation of exchange in the systems Ph_2Hg/R'_2Hg we have also carried out the reaction of diphenylmercury with HgI_2 in the presence of large excess of tetra-n-butylammonium perchlorate or iodide. In accordance with the literature data[13], reaction of Ph_2Hg with HgI_2 is of the second order, irreversible, proceeding at a very high rate, k 24.6 $l \cdot mole^{-1} \cdot sec^{-1}$ at 25°. In agreement with Ingold's data[14] (see, however, ref. 13) on the effect of halide ions in the reactions of dialkyl exchange ($Alk_2Hg/HgBr_2/LiBr$), the reaction rate of Ph_2Hg with HgI_2 decreases sharply in the presence of iodide, and the equilibrium $Ph_2Hg + HgI_2 \rightleftarrows 2\ PhHgI$ installs at 20% conversion. In the presence of iodide ions the equilibrium is shifted to the left with respect to perchlorate because the former slows down the reaction of Ph_2Hg with HgI_2 and probably enhances the disproportionation of PhHgI.

The data obtained undoubtedly testify that in the presence of I^- formation of the complex HgI_3^- slows down the reaction $R_2Hg + HgI_2$. However, there is no definite agreement between the data on the effect of iodide ion in the reactions Ph_2Hg/R'_2Hg (reaction of tetraalkyl type). The results obtained show that the reaction rate of Ph_2Hg with $(PhC{\equiv}C)_2Hg$ in the presence of iodide ions increases while the reaction rate of Ph_2Hg with $Hg(CN)_2$ decreases. Effect of iodide ion may be associated with its ability to complexate with both Ph_2Hg and R'_2Hg. Moreover, the stronger complexes should result with R'_2Hg (mercury being more electrophilic). Certainly, $Hg(CN)_2$ forms stronger complex with I^- than does $Hg(C{\equiv}CPh)_2$. Sequence of such complex formation involves a decrease in electrophilic capability of R'_2Hg, which should lead to the lower exchange rate as it was the case for $Hg(CN)_2$*.

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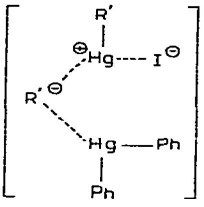
* It should be noted that a ligand exchange and participation of other particles in reaction instead of $Hg(CN)_2I^-$ (for example $HgCNI_2^-$ or HgI_3^-) may take place in the system $Hg(CN)_2/I^-$. However the kinetic dependencies observed for $Ph_2Hg/Hg(CN)_2/I^-$ system markedly differ from those of $Ph_2Hg/HgI_2/I^-$ system.

On the other hand, coordination of I^- with Ph_2Hg should increase a substrate nucleophilic capability and facilitate an exchange. Probably a competitive action of these two factors may explain the observed effect of iodide ion in different systems.

It can be suggested that some other reaction mechanism different from that discussed above may take place in the presence of iodide ion. This may involve preliminary ionization of the complex R'_2Hg with iodide along the R′–Hg bond giving rise to the ion pair $R^-Hg^+{-}R$, and subsequent attack of this pair by a molecule of diphenylmercury:



(II)

Reaction in such case should approach S_E1 mechanism. However, accounting that Ph_2Hg is an exclusively weak nucleophile it could be assumed that the ion-pair attack by diphenylmercury is the slowest step and the reaction is of the second order. Under stationary conditions the following equation holds:

$$\text{Rate} = \frac{k_1 \cdot k_2}{k_{-1} + k_2 \cdot [Ph_2Hg]} \cdot [IP] \cdot [Ph_2Hg]$$

where k_1, k_{-1}, and k_2 are respectively the reaction rate constants of the ion pair (IP) formation, of its reverse reaction and its reaction with Ph_2Hg. If $k_{-1} \gg k_2 \cdot [Ph_2Hg]$, then the rate is $k_{eff} \cdot [IP] \cdot [Ph_2Hg]$.

This mechanism disagrees with the fact that the reaction of Ph_2Hg with $Hg(CN)_2$ is slower in the presence of iodide ion. A proof of the first mechanism was obtained in the study of the reaction of $Hg(CN)_2$ with di-*p*-anisylmercury. Introduction of a strong electron-releasing substituent OCH_3 into diphenylmercury molecule should sharply decrease the reaction rate in the absence of iodide ions. Actually, the rate of reaction between $Hg(CN)_2$ and $(p\text{-}CH_3OC_6H_4)_2Hg$ in the presence of 0.1 *M* Bu_4NClO_4 increases by an order in comparison to that for $Hg(CN)_2$ reacting with Ph_2Hg. In the presence of iodide ions the reaction of $(p\text{-}CH_3OC_6H_4)_2Hg$ with $Hg(CN)_2$ is also faster (Table 5) than reaction of Ph_2Hg.

These results can be interpreted only on the basis of the first mechanism,

TABLE 5

REACTION RATE OF DI-*p*-ANISYLMERCURY WITH $Hg(CN)_2$
DMF, 0.1 *M* Bu_4NI, 25°

$[(CH_3OC_6H_4)_2Hg]_0 \cdot 10^4$ (mole/l)	$[Hg(CN)_2]_0 \cdot 10^4$ (mole/l)	k ($l \cdot mole^{-1} \cdot sec^{-1}$)
5.65	5.65	3.0
8.6	8.6	2.9
5.6	2.8	3.3
6.0	12.0	k_{mean} 3.1

since according to the second mechanism, a decrease in electrophilic tendency on going from Ph_2Hg to $(CH_3OC_6H_4)_2Hg$ leads to the lower reaction rate.

Thus use of the polarographic method makes it possible to study the radical exchange reactions of the completely substituted organomercury compounds in terms of the processes widely employed in the study of electrophilic substitution mechanism.

EXPERIMENTAL

Three diffuse cathodic waves were observed on polarograms of the reaction mixtures. The wave of R'_2Hg appears at the least negative potentials followed by a R'HgPh wave. Finally, a diphenylmercury wave shows itself near −2.5 V. All the waves are two-electronic, corresponding to the processes:

I-st wave $R'_2Hg + 2\,e \rightarrow 2\,R^- + Hg$

II-nd wave $R'HgPh + 2\,e \rightarrow R'^- + Ph^- + Hg$

III-rd wave $Ph_2Hg + 2\,e \rightarrow 2\,Ph^- + Hg$

Concentrations of reagents and reaction products were determined from the values of limiting diffusion current, I_d, *i.e.* from the wave heights using the Ilkovich equation.

Sometime the reduction waves of R'_2Hg and R'HgPh had close potentials. For example, $E_{0.5}$ for $(PhC{\equiv}C)_2Hg$ and $PhHgC{\equiv}CPh$ was 150 mV; thus exact determination of I_d is complicated in such a case and one should use a concealed limiting current technique[15]. However, even with such method the accuracy is as high as 20%.

Kinetic measurements

Ten ml of 0.1 *M* Bu_4NClO_4 or Bu_4NI in dimethylformamide was placed in a polarographic cell thermostatted at 25±0.2°, purged with purified nitrogen. The polarogram of the supporting solution was recorded. Then, 0.05 ml of $2 \cdot 10^{-2}$ *M* solution of one of the components (diphenylmercury, for example) in DMF was added under counter stream of nitrogen, the system was purged with nitrogen for 2 min, and the polarogram of the organomercury compound was taken. The wave height corresponded to the starting concentration C_0. A required quantity of the second component in $2 \cdot 10^{-2}$ *M* solution was further added under counter stream of nitrogen, the mixture was stirred for two min by passing nitrogen, and the polarogram was recorded. Depending on the reaction state, the subsequent polarograms were taken in certain intervals. In case of $(PhC{\equiv}C)_2Hg/Ph_2Hg$ system the reaction rate was calculated from the wave heights of $(PhC{\equiv}C)_2Hg$ and $PhC{\equiv}CHgPh$, in other cases from that of diphenylmercury.

Purification of compounds

Dimethylformamide of "Chistyi" purity grade was shaken with calcinated K_2CO_3 for 72 h, and distilled *in vacuo* (b.p. 38–40°/10 mm).

All the organomercury compounds were recrystallized just before use. Purity of compounds and the mercury halide impurities were controlled by polarography.

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