ON THE MECHANISMS OF SUBSTITUTION REACTIONS OF ORGANOMETALLIC COMPOUNDS

OF NONTRANSITION METALS

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Abstract

The present paper describes results of studies of two types of substi-
tution reactions (mainly of organomercury compounds): $R_nM + M' \longrightarrow R_nM'$ and
$R_{n-p}MX_p + E-X_m \longrightarrow R_{m-q}M'X_q$ (E = M', Hal or H). Various organomercury
compounds readily enter into isotopic exchange reactions with ^{203}Hg. Highly
unstable "organic calomels" apparently are intermediates in these exchange
reactions. Compounds having platinum-mercury bonds are shown to be the first
stage product in the reaction between zerovalent platinum complexes and or-
ganomercury compounds. S_E2, $S_E1(N)$ and $S_E2(i.p.)$ mechanisms are discussed.

$$R_nM + M' \quad \text{EXCHANGE REACTIONS}$$
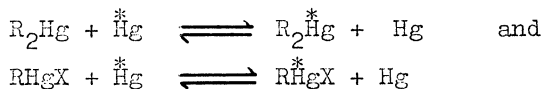
The well-known synthesis of organometallic compounds by the reaction:

$$\frac{n}{2} R_2Hg + M^n \longrightarrow \frac{n}{2} Hg + R_nM$$
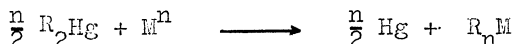
$$(M = Li, Na, Be, Mg, Zn, Cd, Al, Ga, In, Sn, Bi, Te)$$

is extensively used and is frequently the main method of synthesis while
for certain metals it is the only one. The study of the mechanism of these
reactions was for a long time neglected.
    We have examined two of the most simple model reactions of this type
(1, 2, 3):

$$R_2Hg + \overset{*}{H}g \rightleftharpoons R_2\overset{*}{H}g + Hg \quad \text{and}$$

$$RHgX + \overset{*}{H}g \rightleftharpoons R\overset{*}{H}gX + Hg$$

Aromatic, beta-chlorovinyl organomercurials and alpha-oxomercuric com-
pounds readily enter into such isotopic reactions (substitution at aromatic,
olefinic or saturated carbon in the case of the latter compounds). Reactions
proceed in organic solvents under such mild conditions that intermediate
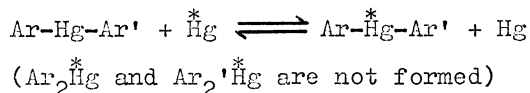formation of free organic radicals is excluded.
    The reaction rate for aromatic compounds
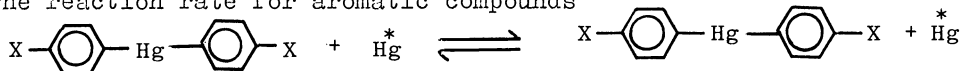
is considerably affected by the nature of X, increasing in the order

$$NO_2 < COOR < Cl < H < Alk < OAlk$$
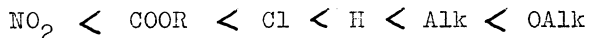
Disproportionation does not occur in the reactions of unsymmetrical compo-
unds with radioactive mercury (1):

$$Ar-Hg-Ar' + \overset{*}{H}g \rightleftharpoons Ar-\overset{*}{H}g-Ar' + Hg$$

$$(Ar_2\overset{*}{H}g \text{ and } Ar_2'\overset{*}{H}g \text{ are not formed})$$

Beta-chlorovinyl compounds react with retention of geometrical confi-
guration (4)

$$
\begin{matrix}
\text{H} & & \text{H} \\
\diagdown & & \diagup \\
& \text{C=C} & \\
\diagup & & \diagdown \\
\text{Cl} & & \text{HgCl}
\end{matrix}
\;+\; \overset{*}{\text{Hg}}
\quad\rightleftharpoons\quad
\begin{matrix}
\text{H} & & \text{H} \\
\diagdown & & \diagup \\
& \text{C=C} & \\
\diagup & & \diagdown \\
\text{Cl} & & \overset{*}{\text{Hg}}\text{Cl}
\end{matrix}
\;+\; \text{Hg}
$$
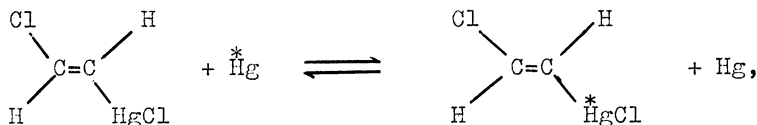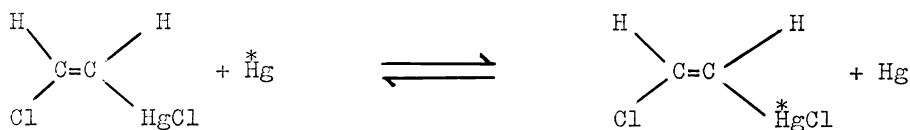
Similar reactions at a saturated carbon atom proceed with complete re-tention of the stereochemical configuration, for instance (2,5):

$$
\begin{matrix}
\text{COOR} & \text{COOR} \\
| & | \\
\text{H}-\overset{*}{\underset{|}{\text{C}}}-\text{Hg}-\overset{*}{\underset{|}{\text{C}}}-\text{H} \\
\text{Ar} & \text{Ar}
\end{matrix}
+\; ^{203}\text{Hg}
\;\rightleftharpoons\;
\begin{matrix}
\text{COOR} & \text{COOR} \\
| & | \\
\text{H}-\overset{*}{\underset{|}{\text{C}}}-^{203}\text{Hg}-\overset{*}{\underset{|}{\text{C}}}-\text{H} \\
\text{Ar} & \text{Ar}
\end{matrix}
+\; \text{Hg}
$$

<div align="center">retention</div>
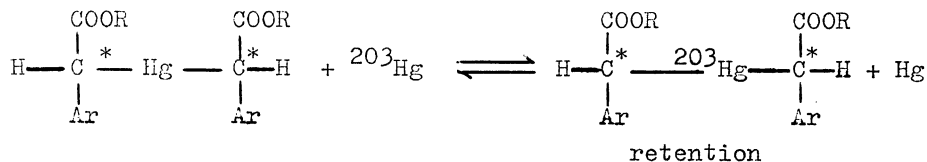
On the basis of the above-mentioned experimental data we have proposed a cyclic transition state

$$
\begin{matrix}
& \text{Hg} & \\
\diagup & & \diagdown \\
\text{Ar} & & \text{Ar} \\
\diagdown & & \diagup \\
& \overset{*}{\text{Hg}} &
\end{matrix}
$$
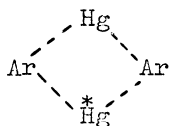
Subsequently, Pollard and Westwood (6,7) carried out a detailed kinetic study of this heterogeneous reaction. They confirmed out data on the example of p-tolylphenylmercury.

It was shown by means of paper chromatography that only the initial compound is present after exchange, no traces of diphenyl- and ditolylmer-cury being detected. By carrying out the reaction under controlled condi-tions the authors were able to achieve an approximately constant degree of fractionation of metallic mercury (constancy of surface) and high reprodu-cibility of kinetic data. The thermodynamic parameters of activation were determined for isotope exchange of 10 R_2Hg-type compounds with metallic mercury in benzene. The reaction rate is in good agreement with the Hammett constant of the substituent (7). For all compounds studied (including di-benzylmercury) an isokinetic relationship is observed (isokinetic tempera-ture - 384°K). This can be considered as an indication of a common mecha-nism. The effect of the substituent at the aromatic ring is typical of S_E2 reactions.

Taking into account changes of hybridization due to substrate solva-tion and the fact that the reaction is interfacial it was proposed to de-pict the transition state as
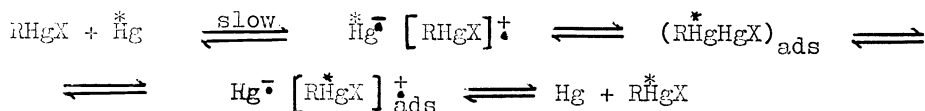
$$
\text{Solv} \diagdown \quad \diagup \text{Solv}
$$
<div align="center">⬡ ─ Hg ─ ⬡</div>
<div align="center">⬡ ⋯ $\overset{*}{\text{Hg}}$ ⋯ ⬡</div>
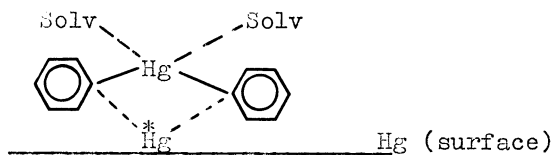
_____ Hg (surface)

Using the pulse electrochemical technique we established that contact of R_2Hg with the surface of metallic mercury leads to formation of "organic calomels" (8):

$$
R_2\text{Hg} + \text{Hg} \;\rightleftharpoons\; R_2\text{Hg}_2
$$
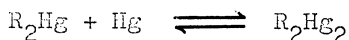
"Organic calomels" are highly unstable$^{*)}$ and their lifetime varies in
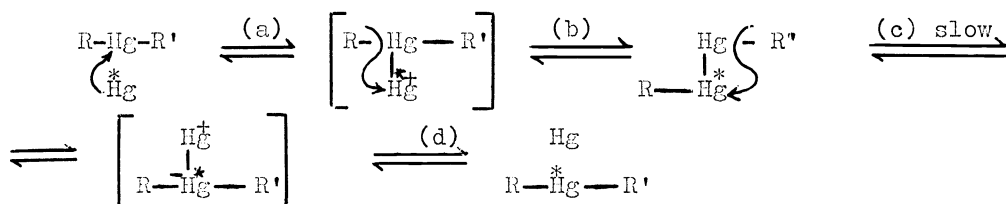
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*) Kreevoy and Walters (9) proposed an oxidation-reduction mechanism as-suming intermediate formation of adsorbed organic calomel, for example,

$$
\text{RHgX} + \overset{*}{\text{Hg}} \;\underset{\text{slow}}{\rightleftharpoons}\; \overset{*}{\text{Hg}}{}^{-}\,[\text{RHgX}]^{+}_{\,\cdot} \;\rightleftharpoons\; (\text{R}\overset{*}{\text{Hg}}\text{HgX})_{\text{ads}} \;\rightleftharpoons\;
$$

$$
\rightleftharpoons\; \text{Hg}^{-}\,[\text{R}\overset{*}{\text{Hg}}\text{X}]^{+}_{\text{ads}} \;\rightleftharpoons\; \text{Hg} + \text{R}\overset{*}{\text{Hg}}\text{X}
$$

Actually, mercury is a reducing and not an oxidizing agent (11).

the range of $10^{-2} - 10^{-4}$ sec depending on R (10).

They apparently are intermediates in the reactions of isotope exchange the mechanism being represented by the following scheme:
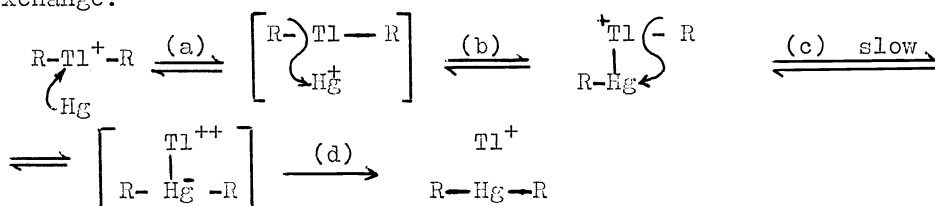
$$R-Hg-R' \xrightleftharpoons{\text{(a)}} \left[R \underset{Hg}{\overset{\ast}{\rangle}} Hg-R' \right] \xrightleftharpoons{\text{(b)}} \underset{R-Hg}{\overset{\ast}{\underset{}{}}} Hg \langle R' \xrightleftharpoons{\text{(c) slow}}$$

$$\xrightleftharpoons{} \left[\underset{R-Hg-R'}{\overset{Hg^+}{\underset{\ast}{\mid}}} \right] \xrightleftharpoons{\text{(d)}} \underset{R-Hg-R'}{\overset{Hg}{\underset{\ast}{}}}$$

Using the galvanostatic method it was shown that the reaction of trans-metalation

$$R_2Tl^+ + Hg \longrightarrow R_2Hg + Tl^+$$
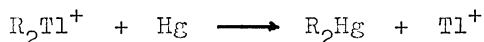
proceeds via the formation of intermetallic cation, RTl^+HgR (11), which is an isoelectronic organic calomel (12).

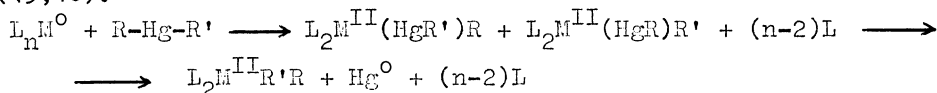The reaction is presumably similar to the above-mentioned isotope exchange:

$$R-Tl^+-R \xrightleftharpoons{\text{(a)}} \left[R \underset{Hg^+}{\overset{}{\rangle}} Tl-R \right] \xrightleftharpoons{\text{(b)}} \underset{R-Hg}{\overset{+}{\underset{}{}}} Tl \langle R \xrightleftharpoons{\text{(c) slow}}$$

$$\xrightleftharpoons{} \left[\underset{R-Hg-R}{\overset{Tl^{++}}{\underset{}{\mid}}} \right] \xrightarrow{\text{(d)}} \underset{R-Hg-R}{\overset{Tl^+}{\underset{}{}}}$$

For surveys of studies devoted to these exchange reaction see ref. (13 and 14).

It may be assumed from the above-described investigation of exchange reaction mechanisms that R_4MHgR-type intermediates are usually formed in reactions of trans-metalation involving metallic mercury or organomercuric compounds.

Proceeding from this assumption we developed a new synthesis of σ-Pt and σ-Pd organometallic compounds. The use of this method is apparently limited only by the availability of the appropriate organomercuric compounds (15,16).
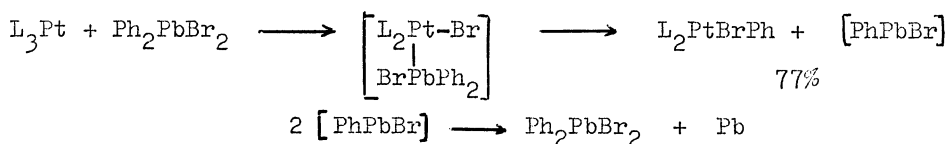
$$L_nM^O + R-Hg-R' \longrightarrow L_2M^{II}(HgR')R + L_2M^{II}(HgR)R' + (n-2)L \longrightarrow$$

$$\longrightarrow L_2M^{II}R'R + Hg^O + (n-2)L$$

Pt:

R	R'	
p-CH$_3$C$_6$H$_4$	Br	
(p-CH$_3$OC$_6$H$_4$)$_2$C=CH	Cl	
CH$_3$OCOCH$_2$	Cl	Yield 50-80%
CH$_3$	Br	
C$_6$H$_5$	C$_6$H$_5$	
C$_5$H$_5$FeC$_5$H$_4$	Cl	

Pd: R = CH$_3$C$_6$H$_4$ R' = Cl

The reactions proceed readily in inert benzene-like solvents at room temperature (under an argon atmosphere).
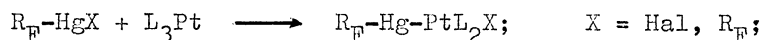
The reaction under consideration turned out to be useful for the synthesis of chelate metallocycles (17).

In the case of a symmetrical organomercuric compound containing chelate-forming groups, a bis-chelate derivative with a "spirane"-type metal atom may be produced as a result of double coordination with elimination of the labile ligand (18). This reaction was carried out for several azoarenes and gave high yields compounds which are difficult to synthesize in any other way.
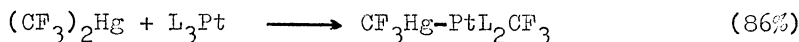
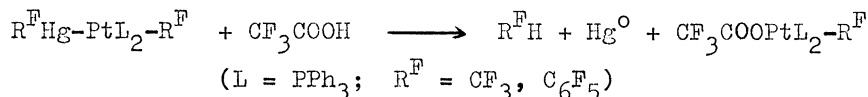Zerovalent platinum complexes react with organolead compounds, too (16):

$$L_3Pt + Ph_2PbBr_2 \longrightarrow \begin{bmatrix} L_2\overset{|}{\underset{|}{Pt}}\text{-}Br \\ BrPbPh_2 \end{bmatrix} \longrightarrow L_2PtBrPh + [PhPbBr]$$
$$77\%$$

$$2\,[PhPbBr] \longrightarrow Ph_2PbBr_2 + Pb$$

Highly stable compounds with a Pt-Hg σ'-bond were synthesized (16,19, 20)

$$R_F\text{-}HgX + L_3Pt \longrightarrow R_F\text{-}Hg\text{-}PtL_2X; \qquad X = Hal, R_F;$$

for instance,

$$(CF_3)_2Hg + L_3Pt \longrightarrow CF_3Hg\text{-}PtL_2CF_3 \qquad (86\%)$$

A characteristic reaction of acidolysis was found (19):

$$R^FHg\text{-}PtL_2\text{-}R^F + CF_3COOH \longrightarrow R^FH + Hg^0 + CF_3COOPtL_2\text{-}R^F$$
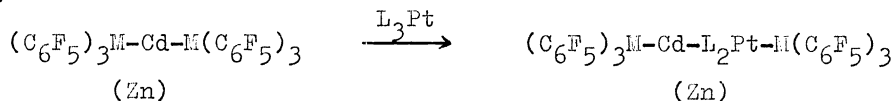$$(L = PPh_3; \quad R^F = CF_3, \; C_6F_5)$$

Hence, complex L_3Pt or the active species L_2Pt^0, corresponding to it, act as a carbenoid, being incorporated at the mercury-element bond. The cis-configuration of $CF_3Hg\text{-}PtL_2CF_3$ is consistent with such an interpretation. The L_2Pt species acts as a nucleophilic carbenoid since the reaction with $(C_6F_5)_2Hg$ proceeds more rapidly than with $(C_6H_5)_2Hg$ (16).

Incorporation of $(Ph_3P)_2Pt$ and $(Ph_3P)_2Pd$ along Hg-Ge and Hg-Sn bonds has been realized (21):

$$(C_6F_5)_3M'\text{-}Hg\text{-}M'(C_6F_5)_3 + M(PPh_3)_n \longrightarrow (C_6F_5)_3M'\text{-}Hg\text{-}M(PPh_3)_2\text{-}M'(C_6F_5)_3$$
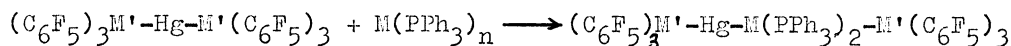
a) M = Pt, M' = Ge;   b) M = Pd, M' = Ge;   c) M = Pt,   M' = Sn.

Compounds with oligometallic chains are very stable (they decompose in boiling trifluoroacetic acid). A stable compound with a Pd-Hg bond was obtained for the first time.

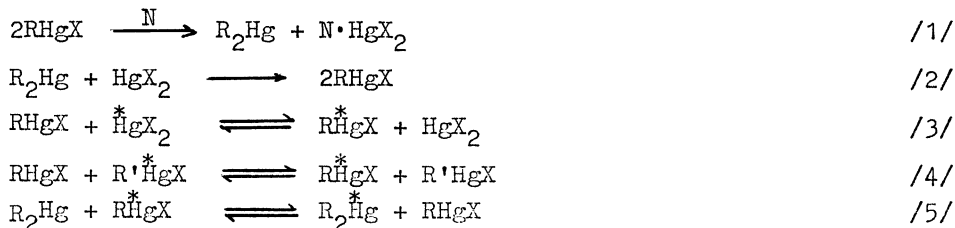Oligometallic chains containing cadmium or zinc were also synthesized (21):

$$(C_6F_5)_3M\text{-}Cd\text{-}M(C_6F_5)_3 \xrightarrow{L_3Pt} (C_6F_5)_3M\text{-}Cd\text{-}L_2Pt\text{-}M(C_6F_5)_3$$
$$(Zn) \hspace{5cm} (Zn)$$

Both sigma-bonds were obtained for the first time (Cd-Pt is stable, Zn-Pt is sensitive to oxygen).

$$R_{n-p}MX_p + E \overset{\frown}{\longrightarrow} X_m \qquad \text{SUBSTITUTION REACTION}$$

S_E2 reactions

Study (22-42) of the kinetics and stereochemistry of electrophilic substitution at a saturated carbon atom (reactions 1-5)

$$2RHgX \xrightarrow{N} R_2Hg + N\cdot HgX_2 \hspace{3cm} /1/$$
$$R_2Hg + HgX_2 \longrightarrow 2RHgX \hspace{3cm} /2/$$
$$RHgX + \overset{*}{Hg}X_2 \rightleftharpoons R\overset{*}{Hg}X + HgX_2 \hspace{2cm} /3/$$
$$RHgX + R'\overset{*}{Hg}X \rightleftharpoons R\overset{*}{Hg}X + R'HgX \hspace{2cm} /4/$$
$$R_2Hg + R\overset{*}{Hg}X \rightleftharpoons R_2\overset{*}{Hg} + RHgX \hspace{2cm} /5/$$

led us to the conclusion that in nonpolar and low-polar solvents the reactions proceed via a cyclic intermediate state (A) (S_{Ei} reactions):

$$R\text{-}HgX + HgZY \qquad \text{(A)} \qquad \longrightarrow RHgZ + HgXY$$

(A)
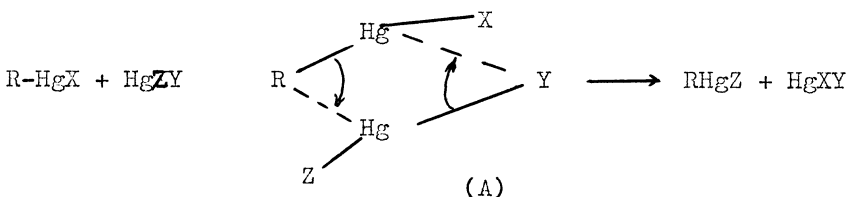
As a rule, stereochemical configuration is retained during S_E2 reactions.

S_E1 (N) reactions

The specificity of S_E1 reactions, known at present, is revealed in the fact that at the rate-determining step the substrate is attacked by a nucleophilic agent present in the solution, while interaction with the electrophile occurs at the fast stage. In the absence of an appropriate nucleophilic catalyst, reactions do not, as a rule, occur or follow an S_E2 route (provided that the nucleophility of radical R and electrophility of the attacking reagent are sufficiently high). Therefore, processes of monomolecular electrophilic substitution should be classified as $S_E1(N)$ reactions. It is assumed that the nucleophilic attack causes ionization of the C-H bond, the equilibrium then being rapidly shifted under the influence of the electrophile.

Anions or neutral molecules (for instance molecules of solvents capable of coordinating with the metal atom of the organometallic compound) may act as the nucleophile N. Finally, the function of the nucleophilic catalyst may be performed by the nucleophilic fragment N of the electrophile E-N. In the latter case it is particularly difficult to distinguish between S_E1 and S_E2 (S_ECi) mechanisms, since formal second-order kinetics should be observed for both mechanisms.

It should be noted that the interpretation of the S_E1 mechanism of reactions of organometallic compounds is very similar to that of the S_N1 mechanism of alkyl halide reactions catalyzed by cations or proton donors, for instance phenol molecules or, in general by protonic solvents.
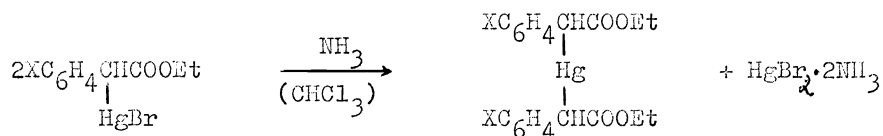
The S_E1 mechanism was first established while studying isotope exchange of α-bromomercuriphenylacetate with $^{203}HgBr_2$ in DMSO (43, 44):

$$PhCH(HgBr)COOEt + \overset{*}{H}gBr_2 \xrightleftharpoons{DMSO} PhCH(\overset{*}{H}gBr)COOEt + HgBr_2$$

The reaction is of the first order with respect to the organomercurial compound and of zero order with respect to mercuric bromide.

At the first stage the organomercuric compound is ionized under the influence of aprotonic dipolar solvents (for instance, DMSO). At the second stage the forming ionic pair rapidly interacts with the electrophile. The ionization degree in the transition state apparently depends on the strength of the nucleophile and the stability of the carbanion of the ionic pair. The rather stable carbanion of phenylacetic ester ($pK_a = 17$) rapidly assumes a planar configuration, thus bringing about racemization.

Previously, while studying symmetrization of the ethyl ester of α-bromomercurphenylacetic acid under the action of ammonia in chloroform

$$2XC_6H_4\underset{HgBr}{\overset{|}{C}}HCOOEt \xrightarrow[(CHCl_3)]{NH_3} XC_6H_4\underset{XC_6H_4\overset{|}{C}HCOOEt}{\overset{CHCOOEt}{\overset{|}{H}g}} + HgBr_2 \cdot 2NH_3$$

it was shown that the reaction is of the second order both with respect to the organomercurial compound and to ammonia /23,24/.
The effect of substituents, however,

$$NO_2 > Hal > H > Alk \qquad \rho = 2.8$$
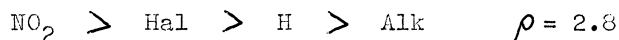
is in contradiction with the S_E2 mechanism (27).

The reaction was assumed to proceed via a four-center transition state in which rupture of the "old" C-Hg bond precedes formation of a "new" carbon-mercury bond. Previously the reaction was assigned to the S_Ei type.

It was shown that if X and Y are substituents with different polar effects, the process rate increases ("cosymmetrization effect") and molecules are arranged in the intermediate state so as to enhance coordination of bromine at the mercury atom (provided that Y is an electron-donor substituent) and rupture of the C-Hg bond (provided X is an electron-acceptor) (31). The presented conceptions accomodate all these finding if the actual mechanism of the reaction is assumed to be $S_E1(N)$ and the function of the nucleophilic catalyst is performed by an ammonia molecule (bearing in mind the coordination capacity of mercury) and by the second molecule of the reagent.
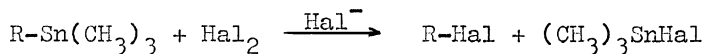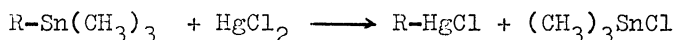
Similarly can be explained the formal second kinetic order and the "anomalous" (from the point of view of the S_E2 mechanism) substituent effect in the reaction of the ethyl ester of α-bromomercuriphenylacetic acid with I_3^- (45). Here I_3^- also acts not only as an iodinating agent but as a nucleo-

philic catalyst as well (S_E1 (I_2^-) mechanism).

The $S_E1(N)$ mechanism for organomercuric compounds was also realized at an ethylenic carbon atom (58-60) and in aromatic compounds (61).

THE ROLE OF IONIC PAIRS IN S_E REACTIONS

Recently we have studied several reactions of mercuro (46,47) and halo-destannylation (48-52) of $RSn(CH_3)_3$ compounds for a wide range of R (R=CH_3, n-C_4H_9, C_6H_5, $C_6H_5CH_2$, CH_2 = $CHCH_2$, CF_3, C_6F_5, $C_6H_5C \equiv C$, C_9H_7 (indenyl), CH_3COCH_2, cyclo-C_5H_5, CN):

$$R-Sn(CH_3)_3 + HgCl_2 \longrightarrow R-HgCl + (CH_3)_3SnCl$$

$$R-Sn(CH_3)_3 + Hal_2 \xrightarrow{Hal^-} R-Hal + (CH_3)_3SnHal$$

Reactions were carried out in methanol, DMSO and carbon tetrachloride.

Several organotin compounds (R = CH_3, n-C_4H_9, Ph, Bz, C_6F_5, CF_3) react in polar solvents according to the S_E2 mechanism. This follows from kinetic data and the character of reactivity variation with the nature of the C-Sn bond.

On the other hand, the absence of a compensation effect and linearity in the change of the free energy in the series of compounds under study indicates continuous change in the structure of the transition state with variation of R, the electrophile and the solvent (48,49).

Quite a different mechanism of iododestannylation is observed for compounds with strong electron-withdrawing groups (R= PhC≡C, C_9H_7, cyclo-C_5H_5, CH_3COCH_2, CN). In this case the least nucleophilic group is cleaved and the reaction rate accelerates to such an extent that we were obliged to apply the stop-flow method (50,52). For R = PhC ≡ C or C_9H_7, the reaction is bimolecular (first order with respect to each component). The reaction rate of both compounds with iodine (as well as with mercury chloride), however, is considerably higher than of iododestannylation of the most S_E2 reactive compounds (PhSn(CH_3)$_3$ and CH_2=CHSn(CH_3)$_3$.

In our opinion these results may be explained by an hypothetical S_E2 mechanism involving contact ionic pairs that are formed at the pre-equilibrium stage and interact with the electrophile at the rate-determining step.

In the case of (CN)Sn(CH_3)$_3$, $CH_3COCH_2Sn(C_2H_5)_3$ and cyclo-C_5H_5-Sn(CH_3)$_3$ the kinetics is even more unusual: first order reaction with respect to the organotin compound and zero-order in iodine. The reaction rate is independent (with the exception of R = cyclo-C_5H_5) of iodide-ion concentration.

Iododestannylation of both these compounds is apparently the first instance of S_E1 mechanism in organotin compounds.

It is assumed that the ionization of the carbon-tin bond proceeds slowly with formation of an ionic pair that then rapidly reacts with iodine.

It should be noted that the postulated participation of ionic pairs in such reactions explains not only the "abnormally" high rate of reactions between these compounds and strong electrophilic substituents, but also enables to unify the S_E mechanism in reactions of organometallic compounds (48):

$$RM \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^-M^+ \xrightarrow[I_2]{k_2} RI + MI$$
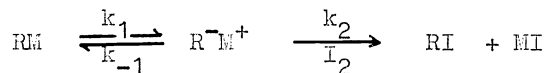
The type of mechanism depends on the ratio of rate constants: the S_E1 mechanism is realized when $k_2[I_2] \gg k_{-1}$; if $k_2[I_2] \ll k_{-1}$ the reaction follows the ion-pair mechanism /$S_E2(R^-M^+)$/.

Compounds with strong electron-donating groups may react according to the classical S_E2 mechanism.

The ionic pair concept was also used to interpret data on iododestannylation in carbon tetrachloride (52).

Reactions of compounds with strong electron-withdrawing groups (R = CN, cyclo-C_5H_5, C_9H_7) are of the second order, first order with respect to the components, and proceed rapidly ($k_2 \sim 10^2 - 10^3$ mole^{-1}. sec^{-1}). The other compounds follow the three-molecular mechanism (second order in iodine), consistent with the behavior of aryltrialkylstannanes (53). These data can be brought into agreement with the S_E2 (R^-M^+) mechanism if we assume formation of contact ionic pairs even in such low-polar solvent as carbon tetrachloride.

Until recently no direct experimental evidence of participation of ionic pairs in the above-described reactions was available. The existence of contact ionic pair and of solventseparated ionic pairs was established

for compounds of alkaline metals, whereas the problem concerning the participation of ionic pairs of heavy metals in S_E reactions remained unclear.

Recently we established the possibility of ionization of R-Sn bonds in R-Sn(CH$_3$)$_3$ compounds in highly solvating solvents by means of spectrophotometric and stereochemical methods (54,55). Compounds R-Sn(CH$_3$)$_3$ (R = 9-phenylfluorenyl, 9-cyanofluorenyl, 3-phenyl-1-methylindenyl) in HMPTA are not only ionized but completely dissociated.

Dissociation was proved by means of spectrometry and conductometry. (9-cyanofluorenyl)Sn(CH$_3$)$_3$ also dissociates in pyridine and acetonitrile and the capacity for dissociation is determined not by the dielectric permeability of the solvent but by its electron-releasing capacity.

Solution of (9-CN-fluorenyl)Sn(CH$_3$)$_3$ in dimethoxyhydrofuran and THF are not electrolites although absorb in the UV region in which the covalent form is inactive (for instance, as compared with the spectrum in hexane). On the other hand, the 9-CN-fluorenyl anion also does not absorb in the same region. Presumably, either complex R-Sn(CH$_3$)$_3$ with the solvent or ionic pair R$^-$$^+$Sn(CH$_3$)$_3$ with small charge separation are formed in DME and THF.

Thus it has been shown that RSn(CH$_3$)$_3$ compounds containing strong electron-acceptor groups are capable of ionization in polar solvents (pK$_a$ of the corresponding RH are in the range of 10-18).

It should be noted that in the case of less electron-negative radicals for instance R = indenyl or p-fluorenyl (pK$_a$ 20-23), there is no absorption in the corresponding UV region in HMPTA. However, ionization for these compounds (not coloured in HMPTA) was established stereochemically (56, 57).

We obtained an optically active 3-methylindenyl organotin compound, that very slowly racemizes in low-polar solvents (hexane, benzene, DME and CH$_2$Cl$_2$, etc.). Addition of HMPTA in very small quantities accelerates racemization (by more than 60 times). It is proposed that racemization occurs at the "return" stage of the ionic pair, RSn(CH$_3$)$_3$, which is formed during coordination of HMPTA at the tin atom:

$$\overset{*}{R}-Sn(CH_3)_3 \rightleftharpoons \overset{*}{R}{}^{-+}Sn(CH_3)_3 \longrightarrow (\pm)R^{-+}Sn(CH_3)_3 \longrightarrow (\pm)R-Sn(CH_3)_3$$
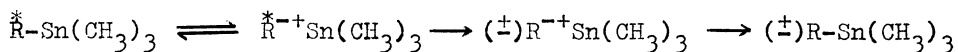
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