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MECHANISM OF REACTIONS OF ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

O.A. Reutov

CONTENTS

1. Introduction 164
2. Bimolecular electrophilic substitution (S_E2) at a saturated carbon atom 164
3. Symmetrisation of organomercury compounds with the aid of diphenylmercury 166
4. Stereochemistry of the S_E2 reactions 166
5. Unimolecular electrophilic substitution at a saturated carbon atom 166

6. Anionic catalysis of one-alkyl isotopic exchange 168
7. Halodemercurations 169
8. Protodemercuration 170
9. "Internal catalysis" in S_E reactions of organomercury compounds 171
10. The reactivity of organomercury compounds of the alkene and aromatic series 173

I. INTRODUCTION

Depending on the electronic nature of the breaking of old bonds and the formation of new bonds, all substitutions can be classified into three groups: nucleophilic substitutions S_N, electrophilic substitutions, S_E, and homolytic substitutions S_R.

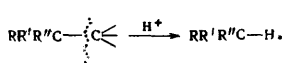
In distinction from the nucleophilic and homolytic substitutions, which have been well studied, the mechanism of electrophilic substitution at a saturated carbon atom was a blind spot in organic chemistry even a decade ago. However, the intensity of the study of the mechanism of this type of reaction is now increasing rapidly.

The reason for this, in addition to interest in the S_E reactions for their own sake, is apparently that as a result of discussion between Ingold and Sven† ideas about the mechanism of nucleophilic substitutions, and in particular S_N1 reactions, were greatly complicated. In this connection there was a natural tendency for a series of great chemists to switch to a study of the mechanism of electrophilic substitutions to try to transfer the regularities thus found to the mechanism of nucleophilic substitution.

To compare ideas about the mechanism of S_E reactions, the first essential is a combined study of their stereochemistry and kinetics, as it is in many other instances.

In distinction from nucleophilic and homolytic substitutions, here above all arises the difficulty of selecting suitable subjects for study, especially as regards stereochemistry. Few such subjects are known as yet.

From 1955 until now Cram (a survey of his work has appeared[3]) has completed a great series of works on the study of the stereochemistry of the reaction for the breaking of a carbon–carbon bond under the action of substances which are proton donors:



As a result interesting facts were obtained on the chemistry of carbanions but in most instances Cram was unable to study the kinetics of the reaction.

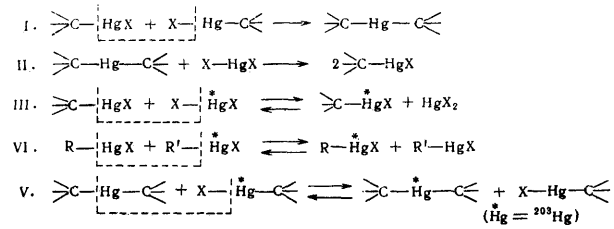
Evidently the most suitable subjects for studying the mechanism of electrophilic substitution at a saturated carbon atom should be organometallic compounds, owing to the definite nature of the polarisation of the metal–carbon bond:



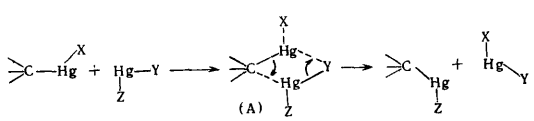
Of all the organometallic compounds, organomercury compounds are the most convenient: they are stable under ordinary conditions but sufficiently reactive, easily prepared, purified, and identified. Therefore, in recent years the most significant progress has been made in studying S_E reactions of organomercury compounds.

2. BIMOLECULAR ELECTROPHILIC SUBSTITUTION (S_E2) AT A SATURATED CARBON ATOM

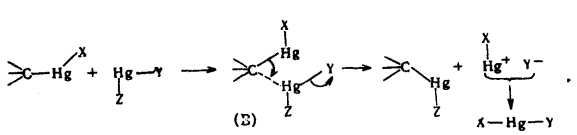
Study of the kinetics and stereochemistry of the electrophilic substitution at a saturated carbon atom of types I–V:



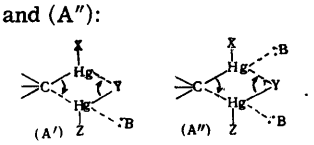
led to the conclusion that in non-polar and low-polar solvents the above reactions pass through the stage of formation of a cyclic four-membered transition state of type (A)[4-7]‡:



(I) X = Y = Hal, Z = Alk; (II) X = Alk, Y = Z = Hal; (III) X = Y = Z = Hal; (IV) Z = Alk, X = Y = Hal; (V) X = = Z = Alk, Y = Hal. The bases for taking such a structure of the transition state are: bimolecular reactions (kinetics of the second order overall and first order with respect to each of the components) proceed with strict retention of the stereochemical configuration, that is, the newly entering metal atom strictly takes the place of that leaving[8-11]; finally, the open transition state of type (B) is improbable in non-polar and low-polar solvents, because it would lead to the intermediate formation of the ions§ HgX^+ and Y^+:



Naturally, with a solvent in whose molecules there are atoms with unshared electron pairs (pyridine, dimethylformamide, ammonia) one or both of the mercury atoms in the transition state should be solvated or even bound by a coordination bond with solvent molecules — the transition states (A′) and (A″):



† The problems have been reviewed.[1,2]

‡ S_E2 reactions which proceed through a stage of a cyclic transition state are often denoted by the symbol S_Ei.

§ It is quite probable that S_E2 reactions proceed through transition state (B) in polar solvents.[12,13]

For the reactions of one-alkyl isotopic exchange (III) and symmetrisation (I) such coordination has been shown experimentally. Thus the isotopic exchange of α-ethoxycarbonylbenzylmercury(II) bromide with mercury(II) bromide in dimethylformamide is really the reaction of R–Hg–X and a complex of HgX_2 with dimethylformamide[14]:

$$R{-}HgX + \overset{*}{H}gX_2\cdot C_3H_7ON \rightleftarrows R{-}\overset{*}{H}gX + HgX_2\cdot C_3H_7ON .$$

Undoubtedly, when the reaction is carried out in pyridine[6,15] the active reagent is $HgX_2.C_5H_5N$, not free HgX_2. The symmetrisation of the same substance under the action of ammonia in chloroform:

$$2R{-}HgX + 2NH_3 \rightarrow R_2Hg + HgX_2\cdot(NH_3)_2,$$

proceeds through the preliminary stage of the formation of a complex of the organomercury compound with ammonia, evidently by scheme 1¶:

Scheme 1

(a) $R{-}HgX + NH_3 \overset{\text{fast}}{\rightleftharpoons} R{-}HgX\cdot NH_3$

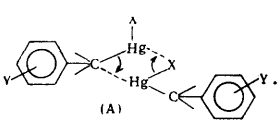
(b) $2R{-}HgX\cdot NH_3 \xrightarrow{\text{slow}} R_2Hg + HgX_2\cdot(NH_3)_2\}\ S_E2.$

Here the S_E2 reaction proceeds through the transition state of type (A").

It is easy to see, however, that general conclusions about the mechanism of the S_E2 reactions at a saturated carbon atom, made in considering the transition state (A). whether or not involving solvation or coordination of mercury atoms, will be identical†, because the transition state (A) will not differ significantly from transition state (A").

The main feature of all these transition states is a four-membered ring (A). This very feature is also responsible for symmetrisation with reactions (II)–(V) and determines the corresponding theoretical conclusions made on the basis of an independent study of S_E2 reactions of all five types. Therefore in judging subsequently the characteristic features of the symmetrisation we will consider for clarity a four-membered cyclic transition state (A), so to speak, "in the pure aspect", having, of course, in mind, that in reality either one or both of the mercury atoms are coordinated to molecules of ammonia.

In studying the influence of structural factors on the rate of symmetrisation of a series of substituted α-ethoxycarbonylbenzylmercury(II) bromides it was concluded that in transition state (A) the breaking of the old C–Hg bond plays a more important part than the formation of the new one[5,6]:



(A)

The values of the rate constants for second-order reactions k_2 are given in Table 1.

The influence of substituents Y on this reaction obeys the Hammett equation. Clearly the order of the influence of the substituents is reversed in comparison with typical

TABLE 1.

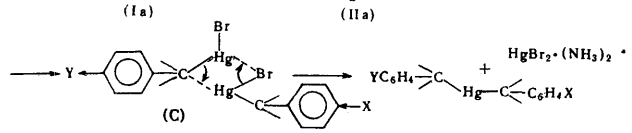
Y	*p*-NO_2	*p*-I	*p*-Br	*m*-Br	*o*-Br	*p*-Cl	*p*-F	H	*p*-CH_3	*m*-CH_3	*o*-CH_3	*p*-C_2H_5	*p*-$(CH_3)_2CH$	*p*-$(CH_3)_3C$
k_2, ml mole^{-1} s^{-1}	17 730	670	540	1445	426	470	148	110	34	71	32	41	42	28

* The constant k_2 was calculated assuming that Hammett's equation is applicable to this series (ρ = 2.85).

S_E2 reactions‡. This feature can be interpreted in the same way, that in consequence of the specific properties of the given organomercury compounds used (high lability of the C–Hg bond), the S_E2 reaction being studied is in the boundary region close to the region of S_E1 reactions unknown until recently (see p. 167).

Since in the transition state (A) not only the old C–Hg bond but also the old Hg–Br bond is broken it is natural to assume that such a type of transition state will be attained more easily for reactions between molecules of different types (Ia) and (IIa):

$$YC_6H_4CH(HgBr)COOR\ (Ia) + XC_6H_4CH(HgBr)COOR\ (IIa) \xrightarrow{2NH_3}$$



(C)

The electron-withdrawing substituent Y should facilitate the breaking of the old C–Hg bond in transition state (C), and the electron-donating substituent X, should facilitate the breaking of the old Hg–Br bond. Therefore such a type of "cosymmetrisation" should be faster than the symmetrisation of either of the two pure substances. Experiment completely confirmed this. Finally, by use of radioactive mercury ^{203}Hg it was shown[24] that a mercury atom from the original molecule (Ia) with a substituent Y preferentially transfers into the complex $HgBr_2.(NH_3)_2$ but an atom of mercury from molecule (IIa) with a substituent X goes into the organomercury compound formed, as can be predicted by starting from the transition state (C):

$$YC_6H_4{-}\underset{(Ia)}{CH(COOC_2H_5){-}\overset{*}{H}g{-}Br} + XC_6H_4{-}\underset{(IIa)}{CH(COOC_2H_5){-}Hg{-}Br} \xrightarrow{2NH_3}$$

$$\longrightarrow YC_6H_4{-}CH(COOC_2H_5){-}Hg{-}CH(COOC_2H_5){-}C_6H_4X + \overset{*}{H}gBr_2\cdot(NH_3)_2$$

where Y = Br, X = H; Y = H, X = CH_3; Y = Br, X = CH_3.

Hence the above cyclic transition state in the S_E2 reactions of organomercury compounds can now be considered adequately proved§.

Note that the work of Dessy and coworkers[28] has suggested the possibility of a more complex transition state in S_E2 reactions at a saturated carbon atom than that proposed by Reutov[4-7] and Ingold[29]. However Dessy's work was not confirmed when checked[30].

¶ The basis for the scheme is given and discussed elsewhere.[16-20]

† Jensen and Rickborn's views on this[20,21] are based on a misunderstanding and are erroneous (see Reutov[22]).

‡ Note that such an "anomalous" influence of substituents is observed in the reaction of esters of α-bromomercuriarylacetic acids with I_2/CdI_2 in toluene.[23]

§ The field of the reactions of organometallic compounds proceeding through an analogous cyclic transitional state, which has been studied, includes some bimolecular electrophilic substitutions of hydrogen, halogen, and metal for metal at saturated, alkene, and aromatic carbon atoms.[18,25-27]

3. SYMMETRISATION OF ORGANOMERCURY COMPOUNDS WITH THE AID OF DIPHENYLMERCURY

Diphenylmercury was proposed[31] as a symmetrising agent for organomercury compounds with a labile C–Hg bond:

$$(C_6H_5)_2Hg + 2R{-}HgX \rightarrow R_2Hg + 2C_6H_5{-}HgX\downarrow,$$

where R = CH_3COCH_2, ClCH=CH, or $ArCH{=}COOC_2H_5$.

Three possible reaction schemes were considered:

Scheme 1

(a) $2R{-}HgX \rightleftarrows R_2Hg + HgX_2$
(b) $(C_6H_5)_2Hg + HgX_2 \rightarrow 2C_6H_5{-}HgX\downarrow$

Scheme 2

(a) $R{-}HgX + (C_6H_5)_2Hg \rightarrow C_6H_5{-}Hg{-}R + C_6H_5HgX\downarrow$
(b) $C_6H_5{-}Hg{-}R + R{-}HgX \rightarrow R_2Hg + C_6H_5HgX\downarrow$

Scheme 3

(a) $R{-}HgX + (C_6H_5)_2Hg \rightarrow C_6H_5{-}Hg{-}R + C_6H_5HgX\downarrow$
(b) $2C_6H_5{-}Hg{-}R \rightleftarrows (C_6H_5)_2Hg + R_2Hg.$

Jensen and Miller[32] thought the last two schemes equally probable. However, on using esters of α-bromomercuriarylacetic acids (R = $ArCHCOOC_2H_5$) labelled with ^{203}Hg it was shown[33] that the reaction mechanism corresponds to scheme 2, but not 1 or 3.

It is easy to see (scheme 2) that both stages of the reaction are completely analogous to the three-alkyl isotopic exchange of organomercury compounds discovered earlier[10,11,34].

4. STEREOCHEMISTRY OF THE S_E2 REACTIONS

All the S_E2 reactions at a saturated carbon atom yet studied by the example of organomercury compounds proceed with strict retention of the stereochemical configuration.

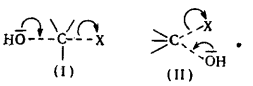
Examples of this are the symmetrisations[8,9] considered above, the three-alkyl isotopic exchange (p. 164, reaction of type V) discovered by Reutov and coworkers[10,11] and somewhat later independently by Ingold and coworkers[34].

Such a reaction of symmetrical organomercury compounds with a mercury halide (p. 164, reaction II) was studied by Ingold and coworkers[35] and by some others.

The S_E2 rule has been formulated[6], according to which bimolecular electrophilic substitutions at a saturated carbon atom proceed with retention of the configuration.

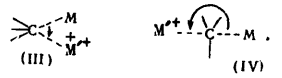
It is important to attempt to answer the following natural question: is the S_E2 rule, which has been developed on the basis of a study of reactivity of only organomercury compounds, generally applicable?

The inversion of the configuration in S_N2 reactions at a saturated carbon atom is known to be due to the fact that of the two possible transition states (I) and (II), the first is energetically more favourable.



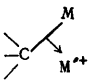
(I) (II)

In a similar fashion, of the two possible transition states (III) and (IV) in S_E2 reactions, state (III) should apparently be more preferable in energetic respects — without even speaking about the stabilisation which is often possible on account of the formation of type (A) rings (see p. 164):



(III) (IV)

By analogy with π-complexes it could be suggested that transition state (III) comes about from the preliminary formation of a σ-complex (V):



(V)

However, unlike the π-complexes, there is still no experimental proof of the existence of such σ-complexes. On the other hand it is difficult to oppose the hypothesis that the formation of transition state (III) precedes the attack by the cation on the C–M bond in the sense of a hypothetical σ-complex (V).

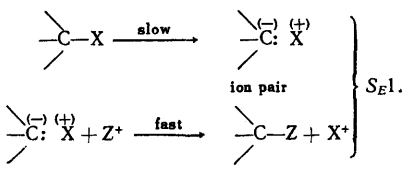
As for spatial factors, they are not very favourable for the retention of configuration for organomercury compounds because of the large covalent and van-der-Waals radii of the mercury atom. Hence the spatial factor which hinders reaching transition state (III) probably cannot change the stereochemical result even for extremely large M and M′.

On the basis of the above it can be suggested that the rule of the retention of configuration in S_E2 reactions can be of a rather general character¶.

5. UNIMOLECULAR ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

Of the four possible mechanisms of heterolytic substitution at a saturated carbon atom (S_N2, S_N1, S_E2, and S_E1) the S_E1 type remained undiscovered until the most recent time.

In the general form the S_E1 mechanism can be expressed as follows:



In the first, slow stage the reaction proceeds by ionisation of the C–X bond with formation of a carbanion (part of an ion pair). In the second, rapid stage of the reaction the ion pair reacts with the electrophilic reagent (Z^+), forming the final compound.

The hope of realising the S_E1 mechanism appeared in connection with the results of stereochemistry and kinetics of symmetrisation of esters of α-bromomercuriarylacetic acids under the action of ammonia.

As noted above, the nature of the influence of the structural factors on the rate of the S_E2 reactions being considered showed that in the transition state (A) the breaking of the old C–Hg bond played a more important part than the formation of the new bond[4,6].

¶ A known instance of the inversion of configuration in an S_E2 reaction of 5-norbornene-2-boronic acid with $HgCl_2$ is explained by the exchange of the boronic acid residue for the HgCl residue being a transannular (and not the usual) electrophilic substitution[36]. Winstein[37] described a similar example.

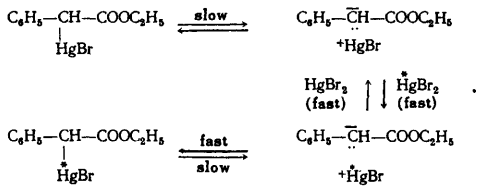
This conclusion, which is unusual for bimolecular reactions, shows that this reaction is close to the boundary region between S_E2 and S_E1 reactions (for the latter, as stated earlier, the stage of ionisation of the old bond is the most important stage)†.

It can be hoped that when the reactions (for the same esters of α-bromomercuriarylacetic acids) are carried out in a solvent with a high ionising ability the S_E1 mechanism will be effected.

Such an attempt, which was crowned with success, was made for the isotopic exchange:

$$RR'R''C{-}HgBr + {}^{*}HgBr_2 \rightleftarrows RR'R''C{-}{}^{*}HgBr + HgBr_2 .$$

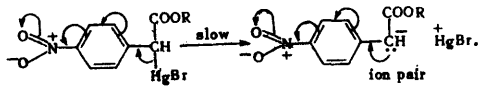
The isotopic exchange in pyridine, dimethylformamide, and ethanol is an S_E2 reaction[15,16]. However, when dimethyl sulphoxide (DMSO), which exhibits high ionising ability, is used as the solvent the kinetics and mechanism of the reaction immediately change. The reaction is first order with respect to the α-bromomercuriarylacetate ester and zeroth-order to the mercury(II) bromide. Hence an S_E1 type of reaction was discovered for the first time[38].



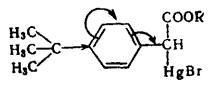
The influence of substituents X in the *para*-position of the benzene ring on the rate of isotopic exchange was studied. The experimental results for substituted α-ethoxycarbonylbenzylmercury(II) bromides at 30° are given in Table 2.

Electron-donating substituents (t-butyl) decrease, but electron-accepting substituents (I, NO_2) increase, the rate of reaction.

Such an order of influence agrees with the predictions about the S_E1 mechanism: electronegative substituents should facilitate breaking of the carbon–mercury bond and stabilise the carbanion, which is formed (as part of an ion pair) as a result of the slow stage of ionisation of the organomercury compound:

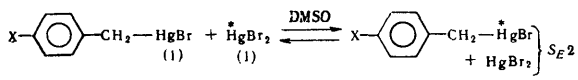


The action of the electropositive substituents will be opposing:



(hence the slow rate of ionisation and consequently of the overall reaction as a whole)‡.

In studying the isotopic exchange in DMSO of benzyl organomercury compounds (less reactive in S_E reactions than esters of α-carboxybenzylmercury(II) bromides) it was found[44] that the reaction takes place by a bimolecular, not a unimolecular, mechanism:



where X = $(CH_3)_2CH$, CH_3, H, Cl, or F, that is, just as when quinoline is used as solvent[45]§.

TABLE 2.

Compounds p-XC_6H_4—CH(HgBr)—$COOC_2H_5$	X		
	$(CH_3)_3C$	I	NO_2
$\frac{k_X}{k_H}$ (DMSO, 30°)	0.71	1.31	4.04

† Note that esters of α-bromomercuriarylacetic acids, like other α-mercurated oxo-compounds, exhibit an extremely labile C–Hg bond, and tend to ionise to a greater extent than the usual alkyl and aryl organomercury compounds.

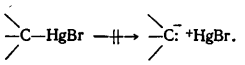
‡ Ingold and coworkers[39] repeated the work of Reutov and coworkers[38,40] and confirmed completely the results about the S_E1 mechanism in the isotopic exchange of α-ethoxycarbonylbenzylmercury(II) bromide with $^{203}HgBr_2$ in DMSO. In addition, they could not reproduce the results of our work[40] in 70% aqueous dioxan, where kinetics of the first order with respect to the organomercury compound and zeroth order in $^{203}HgBr_2$ were observed also (and consequently, an S_E1 mechanism). According to Ingold's results, which he himself considers preliminary, overall second-order kinetics was observed (first in R–HgX and first in $^{203}HgX_2$). Recently Reutov and Sokolov again repeated the work with 70% aqueous dioxan and reproduced their experimental results published earlier[40,41]. The reason for the above differences in the work with dioxan are still not completely clear to the two groups of investigators. This problem, however, no longer is of principal significance, since both Reutov and Ingold[42,43], "agree qualitatively and quantitatively in principle: the S_E1 mechanism is clear in studying the isotopic exchange of α-ethoxycarbonylbenzylmercury(II) bromide with $HgBr_2$ in DMSO" [Ingold's actual words[43] are: "We are agreed, qualitatively and quantitatively, about the fact of main interest; namely that, in anhydrous DMSO, the substitution in α-ethoxycarbonylbenzylmercury(II) bromide by $^{*}HgBr_2$ is of first order in the organo-mercuric salt and of zeroth order in the mercuric salt and hence must have the S_E1 mechanism" (Ed. of Translation)].

§ It is interesting that allylmercury(II) bromide reacts extremely rapidly with $HgBr_2$:

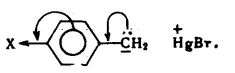
$$CH_2{=}CH{-}CH_2{-}HgBr + {}^{*}HgBr_2 \rightleftarrows CH_2{=}CH{-}CH_2{-}{}^{*}HgBr + HgBr_2 .$$

The isotopic equilibrium is established almost instantaneously at room temperature in various solvents: DMSO, quinoline, acetone, toluene.

Evidently, despite the high ionising ability of DMSO it is here insufficient to ionise the strong C–Hg bond to form an ion pair:



It is natural to assume that the probability of the existence of an S_E1 mechanism of this reaction in DMSO should rise when the carbanion formed as a result of the ionisation exhibits a greater stability owing to the delocalisation of the negative charge, for example, due to structural factors:

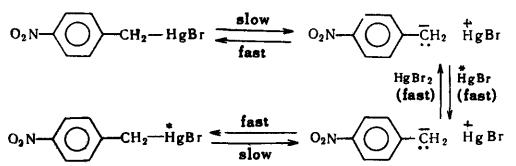


The most suitable subject for the accomplishment of an S_E1 mechanism should be substituted benzylmercury(II) halides with strongly electronegative substituents in the benzene ring. Experimental verification confirmed this prediction.

The kinetics of the isotopic exchange of *p*-nitrobenzylmercury(II) bromide with radioactive mercury(II) bromide in DMSO was studied. As expected, the reaction was of first order overall (first order in organomercury compound and zeroth order to mercury bromide).

Hence an S_E1 reaction of the type being considered was achieved also for benzyl systems, wholly directed by using structural factors and the ionising ability of the solvent[46].

The reaction mechanism can be expressed as follows:



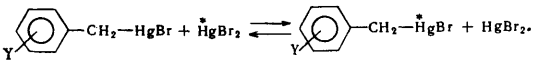
The influence of the halogen X in the compounds $YC_6H_4-CH_2-Hg-X$ on the rate of the S_E1 and S_E2 reactions of isotopic exchange has been studied. It was found that the influence of X is the same in the two instances. The rate of isotopic exchange rises in the sequence: Cl < Br < I.

Such a regularity is understandable, because the more electronegative halogen by induction influence should decrease the effective negative charge on the carbon atom and retard the S_E2 reaction all the same. On the other hand a more electronegative halogen should hinder heterolytic breaking of the C–Hg bond to form a carbanion (retardation of the S_E1 reaction).

Ingold and coworkers[47] described one more example of S_E1 reaction: interaction of di-s-butylmercury with diethylallyl bromide in dimethylformamide, which takes place with racemisation. However, the conclusion about an S_E1 mechanism here seemed erroneous, since no allowance was made in the work for oxidation of the organomercury compound proceeding under the action of atmospheric oxygen[78].

6. ANIONIC CATALYSIS OF ONE-ALKYL ISOTOPIC EXCHANGE

The isotopic exchange of benzylmercury(II) halides with $^{203}HgX_2$ seemed convenient for studying characteristic peculiarities of anionic catalysis discovered by Ingold and coworkers[48] for one-alkyl isotopic exchange:



As shown above, this isotopic exchange takes place in quinoline and dimethyl sulphoxide (with the exception of when Y = NO_2) as an S_E2 reaction:

k_2 (quinoline) = 0.13 litre mole^{-1}h^{-1}; k_2(DMSO) = 0.37 litre mole^{-1}h^{-1}.

In the presence of potassium bromide the isotopic exchange is appreciably faster. For example, at concentrations $[HgBr_2] = [R-HgBr] = 0.06$ M the rate constant of the reaction¶ rises in the following manner as [KBr] is increased[44]:

[KBr], M	0	0.06	0.12	0.18
10^2k_2, litre mole^{-1}h^{-1}	37	148	1444	2139.

The influence of the nature of substituent Y situated in the *para*-position of the benzene ring is opposite for the unactivated reaction and for a reaction catalysed by additions of KBr[44]. Table 3 gives the half-exchange periods $\tau^{1/2}$ in minutes for various $YC_6H_4-CH_2-HgBr$ at [KBr] = = 0, 0.09, and 0.12 M (in DMSO at 70°).

From Table 3 it is evident that in a non-catalysed S_E2 reaction the substituents are arranged in the following sequence as regards accelerating influence:

Cl, F < H < CH_3, $(CH_3)_2CH$.

With isotopic exchange in the presence of KBr the picture changes sharply. In addition to strong acceleration of the reaction there is a change in the influence of the substituent, to the contrary order[44]:

$(CH_3)_2CH < CH_3$, H < F < Cl.

The influence of additions of KBr can be explained by the complexes $HgBr_3^-$ and $R-HgBr_2^-$ being formed in the system:

[(a) $HgBr_2 + Br^- \rightleftarrows HgBr_3^-$; (b) $RHgBr + Br^- \rightleftarrows RHgBr_2^-$],

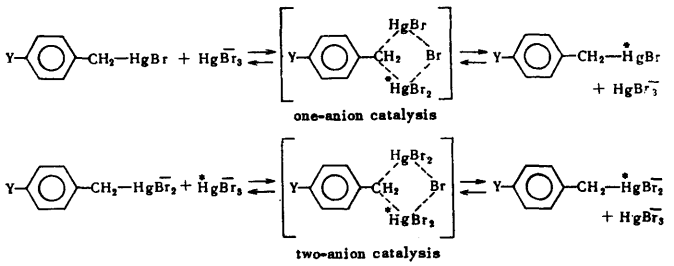
and these complexes are capable of undergoing isotopic exchange. Evidently the second complex should be formed with greater difficulty (that is, at higher KBr concentrations).

TABLE 3.

[KBr], M	$[HgBr_2]$, M	$[YC_6H_4CH_2HgBr]$, M	$\tau^{1/2}$, min for Y =				
			Cl	F	H	CH_3	$(CH_3)_2CH$
0.00	0.06	0.06	1140	1140	1020	780	780
0.09	0.06	0.06	24	35	45	45	50
0.12	0.06	0.06	10	18	25	25	30

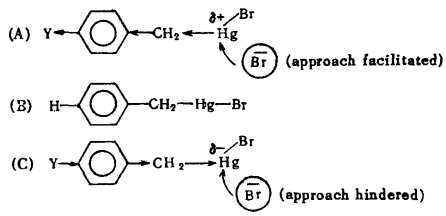
¶ At high potassium bromide concentrations (for example, $[KBr]/[HgBr_2] \geq 2$) k_2 is not maintained sufficiently satisfactorily. This can be explained either by a salt effect or by the fact at relatively high KBr concentrations the reaction can proceed in parallel by the S_E2 and S_E1 mechanisms.

Hence for this isotopic exchange it is evidently necessary to allow for there being two parallel reactions:



If two-anion catalysis is stronger than one-anion catalysis, then the rate of reaction should depend directly on the concentration of the complex $R-HgBr_2^-$. It is evident that substituent Y should affect the ease of formation and consequently also the concentration of this complex.

From this point of view it is understandable why in isotopic exchange catalysed by KBr there is the reverse order of influence of substituents in comparison with the non-catalytic reaction. Naturally the electronegative substituents, which draw off the electron density from the mercury atom, should facilitate the formation of a complex with a bromide anion (in comparison with unsubstituted benzylmercury bromide) (see A):



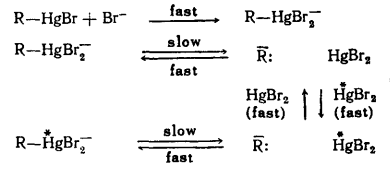
On the other hand, for the electron-donating substituents the formation of a covalent bond of the bromide anion with a mercury atom should be hindered (see B)†.

For isotopic exchange by mechanism S_E1 in the presence of KBr it would be expected that of the two complex formation processes (a) and (b):

$$\text{(a)}\quad HgBr_2 + Br^- \rightleftharpoons HgBr_3^-$$
$$\text{(b)}\quad RHgBr + Br^- \rightleftharpoons RHgBr_2^-$$

only the second, (b), will affect the rate of the reaction, because the ionisation of the C–Hg and $R-HgBr_2^-$ bonds should proceed more readily than in R–HgBr.

The S_E1 mechanism, which is catalysed by KBr, can be represented as follows:

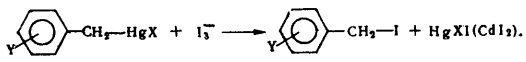


Experiment confirms[49] the above hypothesis of the effect on the reaction rate for only the process of formation of the complex $RHgBr_2^-$.

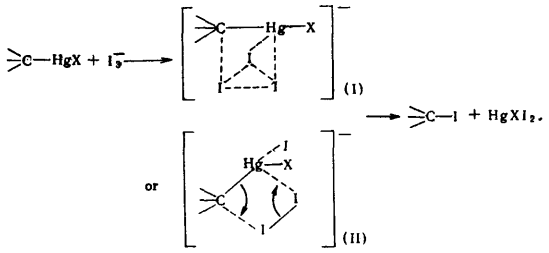
Study of the S_E1 reaction of isotopic exchange of *p*-nitro-benzylmercury(II) bromide with $^*HgBr_2$ in DMSO showed that the reaction rate changes significantly with the KBr concentration. The rate of exchange rises significantly even at KBr concentrations somewhat less than the $^*HgBr_2$ concentration. Thus at [KBr] = 0.05 M, ([$HgBr_2$] = 0.06 M, [RHgBr] = 0.03 M), the rate of exchange increases by a factor of 8. This fact evidently shows that even at KBr concentrations less than the $HgBr_2$ concentration the formation of $RHgBr_2^-$ in the system also takes place to some extent in addition to the formation of $HgBr_3^-$. Naturally a further rise in the KBr concentration rapidly increases the $RHgBr_2^-$ concentration, which should lead to a sharp acceleration of the reaction. At [KBr] = 0.09 M the initial isotopic exchange rate is 47 000 times greater than that in the absence of KBr.

7. HALODEMERCURATIONS

The reaction of benzylmercury halides with iodine in the presence of an excess of cadmium iodide is second-order overall (first with respect to each of the components) in methanol, ethanol, butanol, 70% aqueous dioxan, acetonitrile, dimethylformamide, and dimethylsulphoxide[50-52]. Proof was obtained that I_3^- participates in the reaction (compare Winstein and Traylor[53]):



This S_E2 reaction evidently proceeds through a transition state of type (I) or (II)[52]:



The influence of substituent Y in the benzene ring is shown in Table 4 (k_2 in litre mole^{-1} s^{-1}, in absolute methanol at 19°).

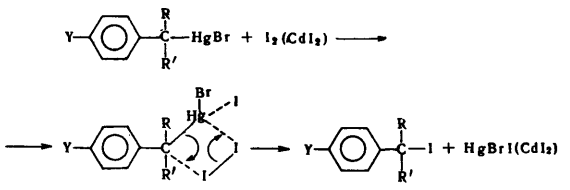
It was noted earlier that the nature of the influence of structural factors on the rate of symmetrisation of esters of α-bromomercuriarylacetic acids shows that in the cyclic four-membered transition state of type (A) the breaking of

TABLE 4.

Y	H	CH_3O	CH_3	F	Cl	Br	NO_2
para	—	8.33	1.93	0.84	0.71	—	instantaneous
meta	0.75	—	0.83	0.42	—	0.46	—
ortho	—	—	1.75	0.22	0.23	—	—

† In principle the possibility of the anion $HgBr_4^{2-}$ (instead of $R-HgBr_2^-$) also participating in two-anion catalysis must be considered. The results of a study[44] of the influence of substituents Y on the reaction rate support the anion $R-HgBr_2^-$, at least for the benzylmercury bromides mentioned above.

the old C–Hg bond is the determining factor. This conclusion is confirmed also for the reaction of α-bromomercuriarylacetic esters with iodine in the presence of cadmium iodide[23]. The reaction was studied in absolute toluene with additions of 1.5 vol.% methanol:



with R = $CO_2C_2H_5$, R′ = H.

The values of the rate constants for a second-order reaction given in Table 5 show that the sequence of the influence of substituents is here analogous to the sequence of the influence for the symmetrisation.

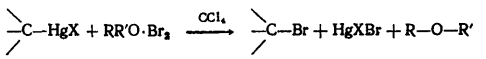
Halodemercuration is somewhat less sensitive to the influence of substitutents (ρ = 2.3) than symmetrisation.

Hence the S_E2 mechanism for the iodination of these compounds is also in a boundary region adjoining the region of reactions which take place by an S_E1 mechanism. This example is again evidence of the arbitrary nature of the division of mechanisms of substitutions into two extreme types.

The reaction of $Ar-CH_2-HgX$ with halogens in the presence of CdX_2 or NH_4X also are S_E2 reactions[54-58].

The reaction of benzylmercury(II) halides with iodine and bromine in the absence of CdX_2 in non-polar solvents (for example, in carbon tetrachloride) is photochemical‡ and proceeds by a radical-chain mechanisms[59,60]. However, small additions of H_2O, ROH, or R_2O in the reaction mixture (0.25 vol.%) alter the kinetics of the reaction of organomercury compounds with bromine (but not with iodine), and consequently also the mechanism itself[62]. For example, irradiation no longer affects the reaction rate. The kinetics of the reaction becomes second-order (first in each of the reagents).

It is natural to assume that this result is due to the formation of a complex of bromine with oxygen-containing molecules and the subsequent participation of this complex in an S_E2 reaction as a donor of electrophilic bromine§:



where R = R′ = H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; R = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, R′ = H.

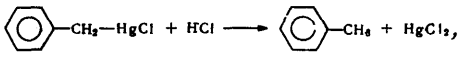
The rate constants for certain reactions in the presence of additions are given in Table 6.

Table 6 shows that the effect of oxygen-containing compounds on the reaction rate can be compared with the "coordination capacity" and electron-donor properties of these compounds.

8. PROTODEMERCURATION

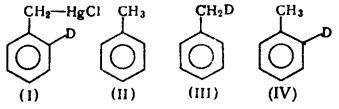
Some features of protodemercuration were studied by the example of benzyl organomercury compounds.

It was shown[63] that in alcohol and dioxan the reaction of benzylmercury chloride (BMC) with hydrogen chloride:



proceeds by an S_E2 mechanism.

In studying the reaction with DCl in dioxan under the conditions of pseudounimolecularity — $[BMC]_0$ = 0.25 M, [DCl] = 2.5 M — it was shown[64] that as the reaction proceeds substances (I), (II), (III), and (IV) appear in the reaction mixture¶:



After the reaction had finished, the reaction mixture naturally contained only compounds (II), (III), and (IV).

TABLE 5.

Y	p-NO_2	p-Br	p-I	p-Cl	p-F	H	m-CH_3	p-$(CH_3)_2CH$	p-$(CH_3)_3C$
k_2, litre mole^{-1} s^{-1}	615*	79.3	43.6	33.4	14.1	10.1	7.1	4.5	3.5

* The reaction is very fast when Y = NO_2, therefore here the constant was calculated assuming that Hammett's equation is applicable to this series.

TABLE 6.

Addition	H_2O	CH_3OH	C_2H_5OH	i-C_3H_7OH	n-C_4H_9OH
k_2, litre mole^{-1} s^{-1}	9.46	3.43	2.73	1.46	1.17

Addition	$(CH_3)_2O$	$(C_2H_5)_2O$	$(C_3H_7)_2O$	$(C_4H_9)_2O$
k_2, litre mole^{-1} s^{-1}	2.44	1.68	0.94	0.87

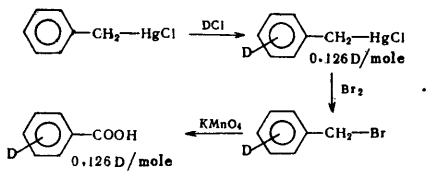
‡ The kinetics, stereochemistry, and mechanism of the homolytic replacement of a mercury atom (connected to a saturated carbon atom) by halogen have been studied by the example of $CH_3CH(HgBr)CH_2CH_3$ with bromine in CCl_4.[61]

§ The reason for the higher reactivity of the $R_2O.Br_2$ complexes in S_E2 reactions compared with Br_2 is given in the section "internal catalysis" (p. 171).

¶ Special experiments showed that the toluene formed does not undergo isotopic exchange with the DCl under the reaction conditions.

From the results given it follows first that BMC undergoes isotopic exchange with the DCl. This is evidently the deutero-exchange observed in organometallic compounds of the transition metals.

That the deuterium was present only in the BMC nucleus was shown as follows:



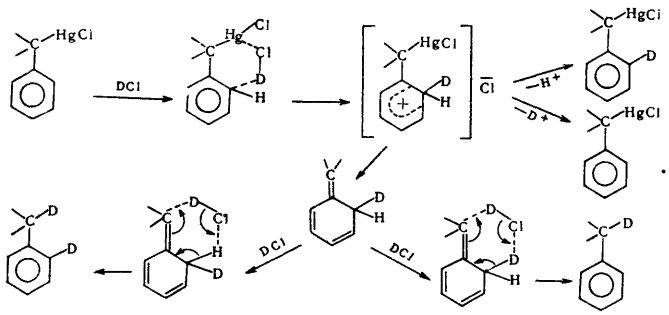
To determine the position of the deuterium in the BMC nucleus it was reduced with $LiAlH_4$ in toluene.



Infrared spectroscopy then showed that dueterium is in practice present only in the *ortho*-position (k_o/k_p = 25 : 1).

Table 7 gives the mass spectra of toluenes isolated at different amounts of conversion of BMC.

Taking all this into account, the mechanism of this rather complex reaction of BMC and DCl can evidently be rather satisfactorily represented by the following scheme [64]:



Bearing in mind the high lability of the C–Hg bond in the dibenzylmercury (DBM) molecules it could be calculated to provide the first example of an S_E1 reaction at a saturated carbon atom in the protolysis of organometallic compounds:

$$(C_6H_5{-}CH_2)_2Hg + HCl \longrightarrow C_6H_5{-}CH_3 + C_6H_5{-}CH_2{-}HgCl.$$

In fact it was shown that in DMSO the reaction proceeds by a first-order dependence and on replacing HCl by DCl the kinetic isotopic effect is absent [65]. This shows that with an overall first-order dependence the reaction has first-order dependence on DBM and zeroth-order on the acid.

TABLE 7.

BMC converted, %	Mass-spectrum of toluenes		
	d_2	d_1	d_0
25	36.4	51.2	12.4
50	36.2	50.2	13.5
70	37.9	48.0	14.0

The simplified mechanism can be represented by the scheme:

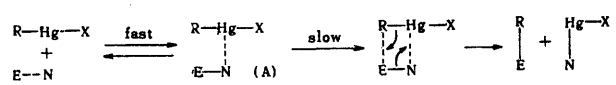
$$(a) \qquad (C_6H_5{-}CH_2)_2Hg \underset{}{\overset{\text{slow}}{\rightleftharpoons}} C_6H_5{-}\bar{C}H_2{:}\overset{+}{H}g{-}CH_2{-}C_6H_5$$

$$(b) \qquad \underset{\text{ion pair}}{C_6H_5{-}\bar{C}H_2{:}\overset{+}{H}g{-}CH_2{-}C_6H_5} + HCl \xrightarrow{\text{fast}} C_6H_5{-}CH_3 + Cl{-}Hg{-}CH_2{-}C_6H_5.$$

It is interesting that this reaction is also first-order in a series of other solvents: dimethylformamide, aqueous (5%) acetonitrile, tetrahydrofuran, butanol. The probable reason is the high lability of the C–Hg bond and also the formation in the reaction of a rather stable ion pair. Some features of the reaction remain inexplicable, for example, the rise in the rate constant k_1 with increase in the HCl concentration.

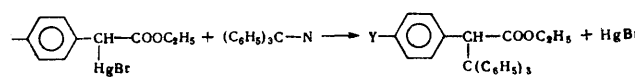
9. "INTERNAL CATALYSIS" IN S_E REACTIONS OF ORGANOMERCURY COMPOUNDS

In all S_E reactions of non-symmetrical organomercury compounds there is acceleration under the action of nucleophilic catalysts. Nucleophilic catalysis, which can be regarded as "external", has been mentioned above (the catalysis of isotopic exchange of organomercury compounds with bases, anionic catalysis, etc.). However, in many instances the catalytic action is connected with the preliminary formation of the complex R–HgX with E–N† of type (A), evidently in the pre-kinetic stage of the reaction. This can be termed "internal nucleophilic catalysis" or "internal nucleophilic assistance". Only after the formation of complex (A) is there the slow stage of the reaction — the formation of a new C–E bond:



The idea of "internal nucleophilic catalysis" in bimolecular electrophilic substitutions has been developed in several papers [66–69].

For example, the mechanism of the triphenylmethylation of ethyl α-bromomercuriarylacetates in dichloroethane has been studied:



where N = Br^-, $HgBr_3^-$, $HgBr_3^-$, ClO_6^-, $SnHal_6^-$.

When N = ClO_4^- there is not reaction, since the formation of a complex of type (A) is impossible. Reaction also does not occur with the strongly ionised compound $2(C_6H_5)_3C^+SnHal_6^{2-}$. The use of a weaker Lewis acid — mercury(II) bromide — even allows the alkylation to be carried out — by the complex $(C_6H_5)_3C^{\delta+}\ldots HgBr_3^{\delta-}$ — although the reaction is slower than for $(C_6H_5)_3C{-}Br$ itself; with the latter it was shown spectrophotometrically that the reaction proceeds through the intermediate formation of the complex $RHgBr.(C_6H_5)_3CBr$.

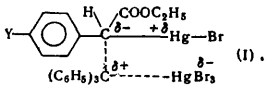
Apparently, in the above reactions the structures of the transitional compounds are different, which is confirmed by the diffferent influence of the substituents Y in the *para*-position of the benzene ring of the organomercury

† E denotes the electrophilic and N the nucleophilic, part of the molecule.

compound. Thus the reaction of mercurated ester with $(C_6H_5)CBr.HgBr_2$ is accelerated by electron-donating and retarded by electron-accepting substituents:

$$C_3H_7,\ C_2H_5 > C_4H_9 > H > F > Cl > Br > I > NO_2.$$

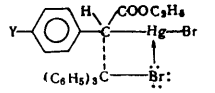
This is evidently connected with the significance of electrophilic attack on a carbon atom — transition state (I):


(I).

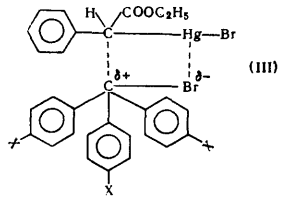
In the reaction of organomercury compounds with trityl bromide itself the influence of substituents Y is the reverse:

$$NO_2 > Hal > H > Alk.$$

The inversion of the influence of the substituents is evidently due to the influence on the reaction rate of the strength of the bond formed between the bromine and the mercury atom — transition state (II). Here it is possible that the determining factor will be the breaking of the old carbon–mercury bond, and not the formation of the new carbon–carbon bond, that is, the reaction mechanism approximates to the S_E1 type:


(II).

The fact that reaction does not occur when completely ionic compounds are used — for example, $(C_6H_5)_3C^+ClO_4^-$ — shows that in any alkylations of the type being considered one can scarcely expect realisation of a completely open structure of transition state (I) and that some fraction of coordination of $HgBr_3^{\delta-}$ with the mercury atom should occur, although less than for structure (II). That both factors — electrophilic attack at a carbon atom and nucleophilic coordination with the mercury atom — are important is also demonstrated by the influence of substituent X in the molecule of the electrophilic agent — transition state (III):

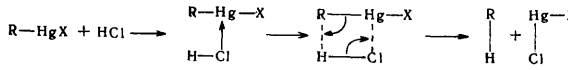

(III)

where X = CH_3, H, NO_2.

For example, the alkylation rate decreases on going from trityl bromide to tritolylmethyl bromide, that is, on reducing the positive effective charge on the carbon atom. However, a decrease in the effective negative charge on the bromine atom of the triarylmethyl bromide also hinders reaction. It was shown that tri-(*p*-nitrophenyl)methyl bromide, in which the carbon–bromine bond is more covalent than in trityl bromide generally does not alkylate a mercurated ester. Hence for trityl bromide there is an optimal combination of conditions which is responsible for the good alkylating ability of this substance. These results are good illustrations of the necessity for nucleophilic coordination in reactions of organomercury compounds‡.

An analogous regularity can be demonstrated by the example of the protolysis of organomercury compounds.

Reutov and coworkers[63] and Dessy and coworkers[71] showed that the rate of protolysis of organomercury compounds by hydrogen chloride decreases on raising the concentration of water in the solvent. This phenomenon is connected with the fact that at low water concentrations a rise in its concentration is accompanied by an increase in the solvation of HCl and its deactivation, but at higher water concentrations there is a simultaneous ionisation of the HCl, which also hinders the reaction. In addition to the other arguments (the absence of reaction with strong acids incapable of coordination with mercury, for example, $HClO_4$), this observation confirms the hypothesis that the reactant is not the solvated proton but the molecular form HCl, most probably its ion pair. In this it is possible that the nucleophilic coordination of chlorine with mercury occurs in the pre-kinetic stage and then is accompanied by electrophilic attack of hydrogen on carbon:



Naturally, as a result of this, a cyclic transition state is realised in the reaction. Possibly the formation of such a structure of a transition state is an important factor facilitating the strict retention of the stereochemical configuration in reactions of the S_E2 type.

It can be hoped that the conception of internal nucleophilic association will be quite helpful in organoelemental chemistry. Even now much of what was incomprehensible earlier has received a simple and natural explanation§ from the standpoint of this conception.

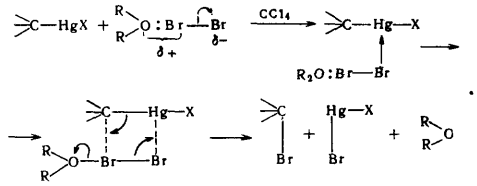
For example, it was not understood earlier why the complexes of bromine with ethers $R_2O.Br_2$ are more effective reagents in S_E2 reactions with organomercury compounds than free [62]bromine (see p. 170).

Taking into account the necessity for internal nucleophilic association this is easy to understand: in the complex $R_2O.Br_2$ the electron density at one of the bromine

‡ The part of nucleophilic coordination in the reactions of organomercury compounds of the aromatic series is evidently less significant. Thus in the triphenylmethylation of arylmercury bromides for both the complex $(C_6H_5)_3CBr.HgBr_2$ and the free $(C_6H_5)CBr$ the transition states probably have an open structure[70].

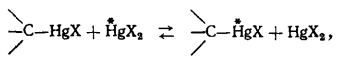
§ "External nucleophilic catalysis" in S_E reactions also receives steady attention from this standpoint. Allowing for this phenomenon we will reconsider some generally accepted positions. For example, the widely accepted view that symmetrical organomercury compounds R_2Hg are more reactive than the organomercury salts RHgX is true only for non-catalytic reactions. Under catalytic conditions (when R_2HgX^- and $RHgX_2^-$ really react) the reactions of fully substituted organomercury compounds and of organomercury salts are accelerated but for the latter compounds the acceleration is considerably greater. As a result under catalytic conditions the organomercury salts react more rapidly than symmetrical organomercury compounds.

atoms is higher than on the bromine atoms in the Br_2 molecule. Hence the greater capability to coordination with mercury atoms:

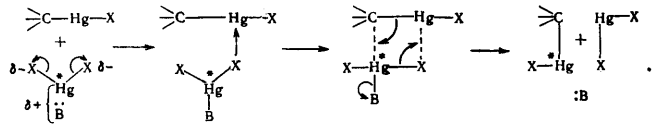


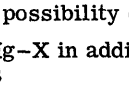
The S_E2 reaction becomes so fast that the competing process — photochemical, free-radical reaction — is suppressed.

In reactions of monoalkyl isotopic exchange:



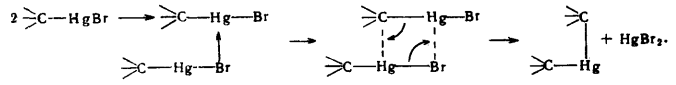
the catalytic action of bases can be explained by the greater tendency of the halogen atoms in $B.\overset{*}{H}gX_2$ complexes to nucleophilic association:



Finally the possibility of the formation of complexes of the type  in addition at a considerable excess of a base must be considered. Here the internal nucleophilic association will be hindered but reaction by an S_E1 mechanism will simultaneously be facilitated.

When the necessity of nucleophilic association is borne in mind it is not surprising that halodemercuration (p. 169) by the S_E2 mechanism takes place easily under the action of the nucleophilic reagent I_3^-,[50-52] etc.

We note, finally, that in the previously considered symmetrisation of organomercury compounds it seems completely possible that the formation of a four-membered cyclic transition state also precedes nucleophilic coordination of a bromine atom with mercury in the pre-kinetic stage:



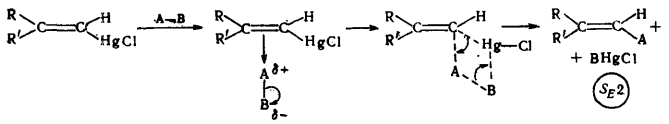
10. THE REACTIVITY OF ORGANOMERCURY COMPOUNDS OF THE ALKENE AND AROMATIC SERIES

As is well known, in general the mechanism of substitutions in saturated, alkene, and aromatic carbon atoms differs significantly.

However, in organomercury compounds it is impossible not to note in the S_E reactions a known similarity due to a general, extremely characteristic replaceable group (HgX, sometimes HgR).

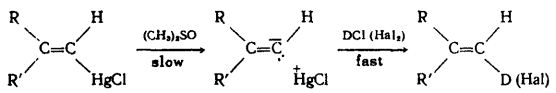
The S_E2 reactions of alkene and aromatic organomercury compounds in low-polar solvents apparently also proceed through a cyclic four-membered transition state[72-77].

For example, the S_E2 reaction of *cis*- and *trans*-β--chlorovinylmercury(II) chlorides and the *cis*- and *trans*--isomers of styrylmercury halides proceed with retention of the configuration[72-74,77]; their mechanism can be represented by the scheme:



(I) R=Cl, R′=H; (II) R=H, R′=Cl,
(III) R=C_6H_5, R′=H; (IV) R=H, R′=C_6H_5

It is interesting that the S_E1 reaction at an alkenic carbon atom also proceeds with retention of the geometrical configuration[73,74]:



The mechanism of protolysis and halodemercuration of aromatic organomercury compounds also has several similar features[75,76] with the mechanism of the same reactions in the aliphatic series.

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