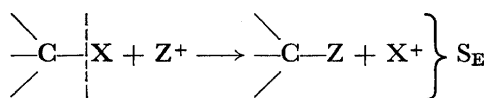


# THE IMPORTANCE OF COORDINATION IN ELECTROPHILIC SUBSTITUTION REACTIONS OF ORGANOMETALLIC COMPOUNDS

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The mechanism of electrophilic substitution at a saturated carbon atom

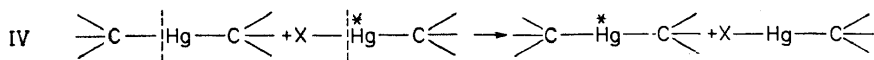
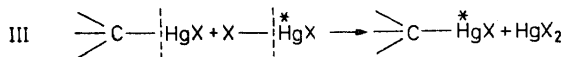
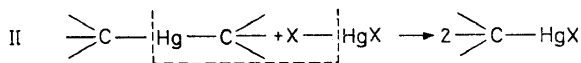
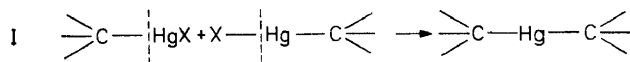


has been clarified by recent work on organometallic compounds<sup>1-3</sup>. This is largely because of the polarization of the metal-carbon bond  $\overset{\delta-}{\text{C}}-\overset{\delta+}{\text{Me}}$ , which favours  $\text{S}_E$  reactions.

Organomercury compounds are most convenient for such studies. They are stable under normal conditions, fairly reactive, and easy to obtain and identify.

## BIMOLECULAR ELECTROPHILIC SUBSTITUTION

We studied first of all the following four types of electrophilic substitution reactions:



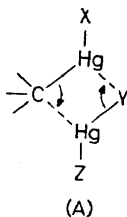
(\*Hg = <sup>203</sup>Hg)

All reactions are bimolecular and are carried out in non-polar and less polar solvents (without the participation of free ions) with strict retention of



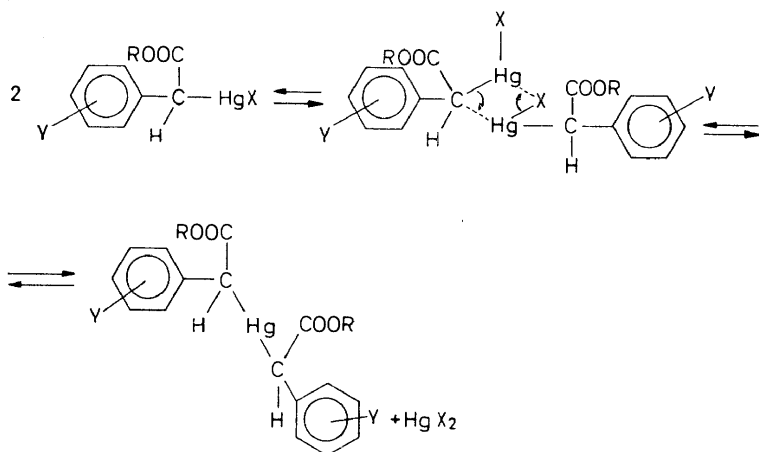
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However, for the sake of simplification we will consider a cyclic transition state, say in "pure state" (A). We must also remember that in many cases



one or both mercury atoms are coordinated by the solvent.

The  $S_E2$  reactions are substantially affected by polarization of the participating substances, an effect thoroughly confirmed<sup>5, 12, 13</sup> in studies of the ammonia-induced symmetrization of ring-substituted  $\alpha$ -bromomercury-arylacetic esters (the ring substituent Y was varied):



The results obey Hammett's equation (Figure 1). The effect of substituents Y have a strong effect on the rate of symmetrization (cf. Table 1).

Table 1. Effect of substituents Y on the rates of symmetrization  
 $YC_6H_4-CH(HgBr)-COOC_2H_5$

Y	p-NO <sub>2</sub>	p-I	p-Br	m-Br	o-Br	p-Cl	p-F	H	p-CH <sub>3</sub>	m-CH <sub>3</sub>	o-CH <sub>3</sub>	p-C <sub>2</sub> H <sub>5</sub>	p-(CH <sub>3</sub> ) <sub>2</sub> CH	p-(CH <sub>3</sub> ) <sub>3</sub> C
$K_2, \text{ml.mole}^{-1}.\text{sec}^{-1}$	17,730	670	540	1445	426	470	148	110	34	71	32	41	42	28

We thus come to the conclusion that in the  $S_E2$ -reaction under investigation the breaking of an existing C—Hg bond is more important than the formation of a new one. Since not only the C—Hg bond but also the Hg—Br

bond is broken in the formation of the transition state (A), one might expect the symmetrization to be faster in the reaction of two organomercury salts containing different *para*-substituents on the ring.

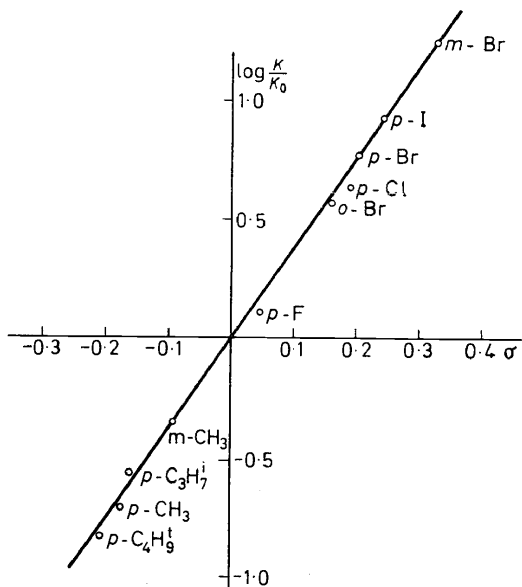
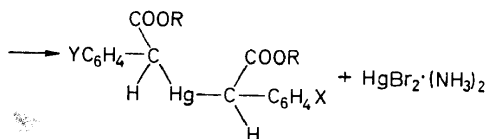
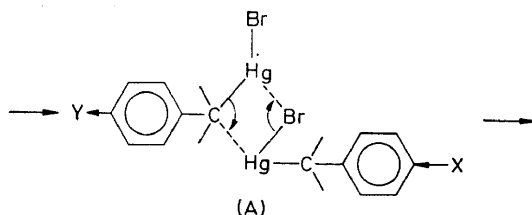
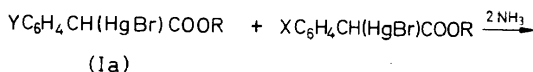


Figure 1. Application of Hammett's equation to kinetics of symmetrization of  $p\text{-YC}_6\text{H}_4\text{CH}(\text{HgBr})\text{COOC}_2\text{H}_5$

Thus if Y is an electron acceptor and X an electron donor, the transition state (A) will be formed more readily than in the reaction of two identical molecules, facilitating the fission of the existing C—Hg bond in the first case and that of the Hg—Br bond in the second:



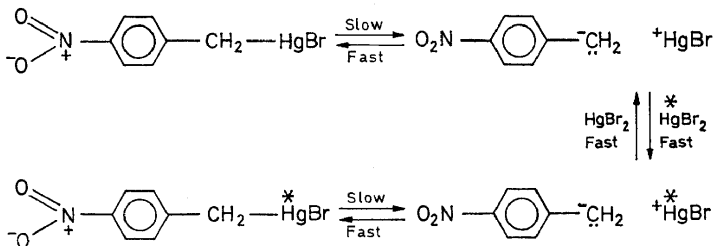
The initial rates of such cosymmetrization were determined when the Y and X groups were respectively H and Cl, H and Br, CH<sub>3</sub> and H, CH<sub>3</sub> and





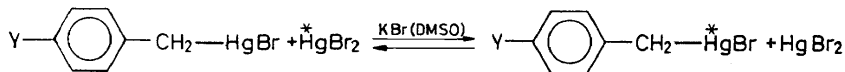
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Only in the case of *p*-nitrobenzylmercuric bromide using DMSO as the solvent, we could realize S<sub>E</sub>1-mechanism<sup>22</sup>:



## NUCLEOPHILIC CATALYSIS IN S<sub>E</sub>-REACTIONS

The phenomenon of electrophilic catalysis in S<sub>N</sub>-reactions at saturated carbon was studied exhaustively but the nucleophilic catalysis in S<sub>E</sub>-reactions was not studied until recently. We studied this phenomenon using one-alkyl isotope exchange reaction of benzylmercuric bromides with HgBr<sub>2</sub> in DMSO as a model. The reaction was found to be strongly catalysed by anions (such as halide ions) which are known to coordinate with mercuric salts. The catalysed reaction is generally of the form:



In the solvent dimethylsulphoxide, second order kinetics are observed.

The acceleration in rate produced by added bromide ions shows that the reaction is still an independent process, and not a combination of two steps of the two-alkyl exchange, since the two-alkyl exchange is known to be strongly retarded by halide ions<sup>23</sup>.

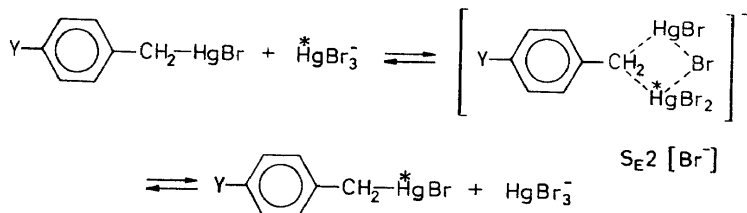
The magnitude of the catalysis can be for instance illustrated by the following data<sup>21</sup>

[KBr], mole l <sup>-1</sup>	0	0.06	0.12	0.18
10 <sup>2</sup> K <sub>2</sub> , l. mole <sup>-1</sup> h <sup>-1</sup>	37	148	1444	2139

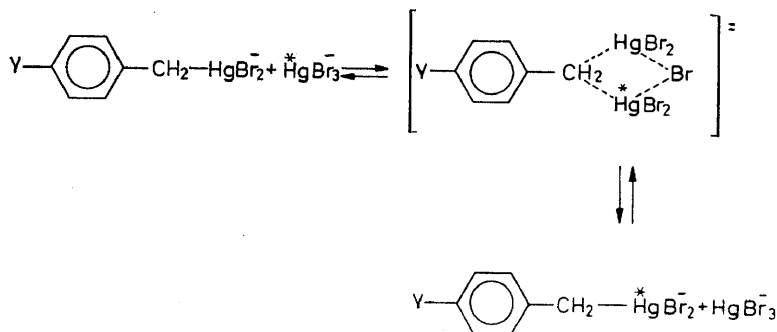
If the two reactant concentrations are kept constant ([RHgBr] = [HgBr<sub>2</sub>] = 0.06), then the second order rate constant, K<sub>2</sub>, increases linearly with increasing bromine ion concentration [Br<sup>-</sup>] up to the point where [Br<sup>-</sup>] = 0.06. At this point there is a sharp change in gradient, although the relationship between [Br<sup>-</sup>] and K<sub>2</sub> continues to be linear. This change at [Br<sup>-</sup>] = 0.06 indicates that two types of catalysis are operative. No further change in gradient is observed at [Br<sup>-</sup>] = 2 × 0.06.

The observed catalysis is too large to be explained in terms of a normal salt effect; it indicates the incursion of a new mechanism in which one or more of the added bromide ions are involved in the rate-determining step. At low concentrations of the added anion ([Br<sup>-</sup>] < 0.06), only one anion is involved in the rate-determining step. These two forms of catalysis are distinguishable kinetically, and have been called by Ingold<sup>24</sup> as the "one-anion" and "two-anion" catalysed reactions.

It is usually believed that the bromide anion complexes strongly with  $\text{HgBr}_2$ , but only very weakly with  $\text{RHgBr}$ . For the reaction under study, however, the halide ion complexes strongly with  $\text{HgX}_2$  in the initial state, but even more strongly in the transition state where it acts as a bridge between a partially formed  $\text{HgX}_2$  molecule and a partially formed  $\text{HgX}_3^-$  ion. The overall result is a larger increase in rate.

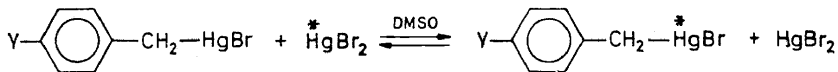


When the concentration of added anion exceeds the reactant concentration ( $[\text{Br}^-] > 0.06$ ), a second anion is involved in the rate-determining step. The suggested transition state for this "two-anion" catalysed reaction is shown below:



In the reaction under study the two-anion catalysis is stronger than the one-anion catalysis†.

The influence of the substituents Y on the rate of the non-catalysed reaction and of the two-anion catalysed reaction is different:



without  $[\text{Br}^-]$ :  $\text{Y} = \text{Alk} > \text{H} > \text{Hal}$

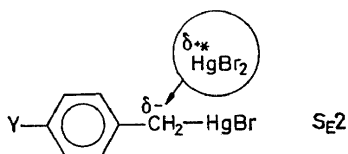
$[\text{Br}^-] = 2[\text{RHgBr}]$ :  $\text{Y} = \text{Hal} > \text{H} > \text{Alk}$

This inversion in the influence of the substituents can be explained if we take into consideration that for the first reaction the value of  $\delta^-$  on the carbon

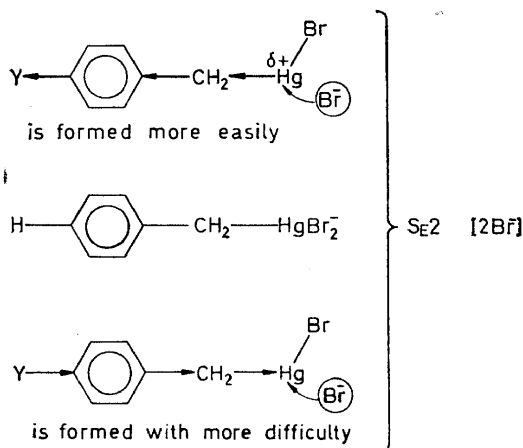
† In general, it is not possible to predict whether the two-anion catalysis is stronger or weaker than the one-anion catalysis. In fact both types of behaviour are observed<sup>24</sup>.



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atom is important whereas for the two-anion catalysed reaction the ease of formation of the anion  $RHgBr_2^-$  is very important which depends on the value of  $\delta^+$  on the mercury atom:

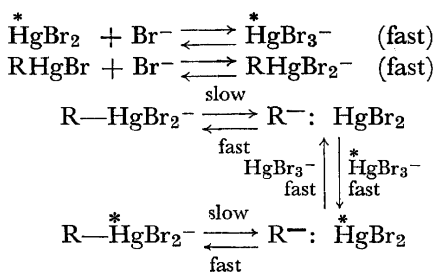


The influence of the bromide anion on the rate of  $S_E1$ -reaction is even stronger than on the rate of  $S_E2$ -reaction, for instance:

[HgBr <sub>2</sub> ]	[RHgBr]	[KBr]	$K_1$
0.06 mole l. <sup>-1</sup>	0.03 mole l. <sup>-1</sup>	0.00 mole l. <sup>-1</sup>	1
0.06 mole l. <sup>-1</sup>	0.03 mole l. <sup>-1</sup>	0.05 mole l. <sup>-1</sup>	8
0.06 mole l. <sup>-1</sup>	0.03 mole l. <sup>-1</sup>	0.09 mole l. <sup>-1</sup>	47,000

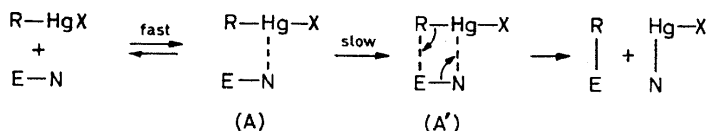
R = O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-; in DMSO

The proposed mechanism of this  $S_E1$  [2Br<sup>-</sup>] reaction is shown below:

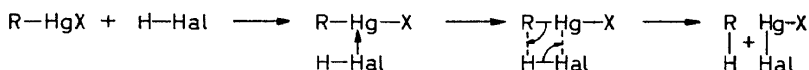


### NUCLEOPHILIC ASSISTANCE IN $S_E2$ -REACTIONS

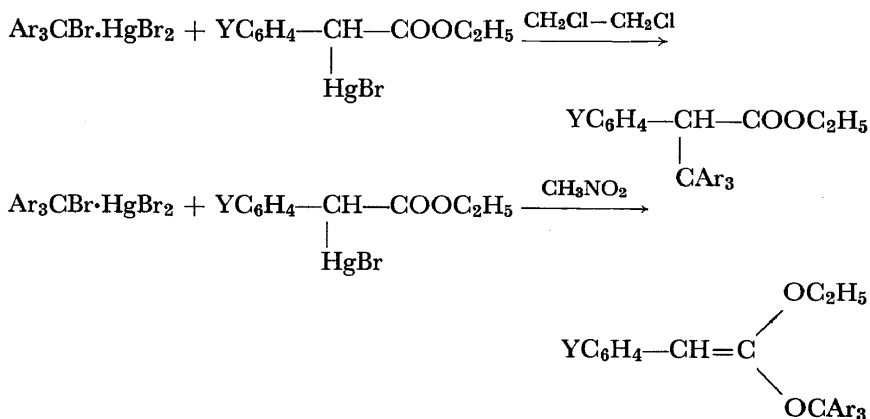
The work of some authors<sup>25-27</sup> has shown that in the reaction of organomercury compounds a role of considerable magnitude is played by the opportunity for nucleophilic assistance, e.g. preliminary coordination of mercury atom of the  $RHgX$  by the nucleophilic part of the reacting molecule  $EN$  (intermediate A). This results in the formation of a cyclic transition state ( $A'$ ) in which nucleophilic attack on the mercury atom and electrophilic attack on the carbon atom is carried out simultaneously by different parts of the attacking agent. It is also possible that the nucleophilic attack on the mercury atom precedes the rate-determining step.



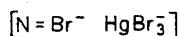
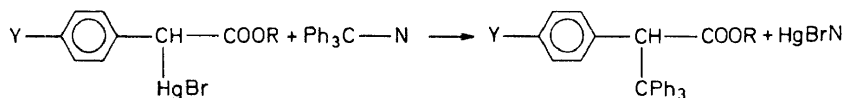
The study of protolysis of organomercury compounds by  $HCl$  in organic solvents showed that the rate of reaction decreases with the increase in water content of solvents. This means that the reacting agent is a non-ionized molecule  $HCl$ <sup>28, 29</sup>.



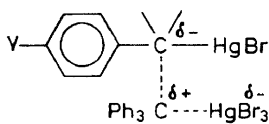
Reaction with  $HClO_4$  does not occur at all because of the absence of the tendency of  $HClO_4$  towards coordination with mercury atom (nucleophilic assistance). The alkylation of organomercury compounds with triaryl bromomethane was studied<sup>27</sup> taking into consideration the idea of nucleophilic assistance. It was previously shown<sup>30</sup> that depending on the nature of the solvent the reaction of triphenyl bromomethane and of its complex with mercuric bromide with the ethyl ester of  $\alpha$ -bromomercuriphenylacetic acid takes place either exclusively at the carbon atom (in dichloroethane) or practically exclusively at the oxygen atom, i.e. with transfer of the reaction centre (in nitromethane):



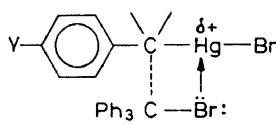
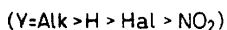
Moreover, it was found that with either solvent, the addition of mercuric bromide to the reactants leads to a decrease in reaction rate<sup>31</sup>. It is known that complexes of alkyl halides with Lewis acids are more highly ionized and are stronger alkylating agents than are alkyl halides themselves. According to the data of Skoldinov and Kocheshkov<sup>32</sup>, organometallic compounds are no exception. Thus, alkylation and acylation of organomercury and organotin compounds are greatly facilitated by the presence of aluminium chloride. Therefore, our result showing that the reaction is inhibited by mercuric bromide is anomalous. In addition, it was found that the reaction does not generally take place in the presence of a stronger Lewis acid, such as stannic chloride, which forms the ionized compound  $[(C_6H_5)_3C^+]_2SnX_6^{2-}$  with triphenylbromomethane. Negative results were also obtained when the completely ionized triphenylmethyl perchlorate was used.



Hence, it follows that transition states of different structures are formed with different alkylating agents, the cyclic structure (II) is formed in the case of triphenylbromomethane and the non-cyclic structure (I) results in the case of its complex with mercuric bromide.



(I)



(II)



These cases turned out to differ kinetically also. The reaction of the organomercury compound with the complex  $(C_6H_5)_3CBr \cdot HgBr_2$  is of the second order; in the case of tribromomethane itself, a complex with a molecule of the organomercury compound is formed before the rate-determining step, and this complex then reacts intramolecularly in accord with a first order rate law<sup>31</sup>. The effect of substituents in the molecule of organomercury compound also differs in these two cases. In reactions of the complex  $(C_6H_5)_3CBr \cdot HgBr_2$  with substituted mercuriated esters, the order of the effect of substituents is that usually observed in electrophilic substitutions, specifically, electron-donor substituents promote the reaction, while electron-acceptor substituents retard it<sup>31</sup>. The effect of substituents is completely reversed in reactions with triphenylbromomethane itself. It may be assumed that this fact is associated with the effect of the substituents on the strength of the  $\text{Br} \rightarrow \text{Hg}$  coordination in the resulting complex. It should be mentioned that for all complexes formed, the optical density of the solutions (obtained by extrapolation of the kinetic curves  $d = f(\tau)$  to  $(\tau \rightarrow 0)$ ) is the

same at different concentrations regardless of the nature of the substituent in the organomercury compound. Therefore, we may not speak of different amounts of complex, but only of differences in the strength of the bromine-mercury bond in the complexes. In this case, the rate-determining factor is apparently scission of the C—Hg bond, and the mechanism of this reaction is most probably intermediate between  $S_E2$  and  $S_E1$ . In any case, it is a fact that the effect of substituents changes under conditions favourable to nucleophilic coordination.

Since, however, the ethyl ester of  $\alpha$ -bromomercuriphenylacetic acid does not react with  $(C_6H_5)_3CClO_4$  or with  $(C_6H_5)_3CBr \cdot SnCl_4$ , it cannot be assumed that in the case of  $(C_6H_5)_3CBr \cdot HgBr_2$  transition state (I) represents an extreme case of a completely open system, since even an increase in the electrophilic properties of the reagent, under conditions such that coordination at the mercury does not occur at all does not make alkylation possible.

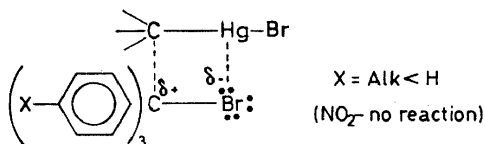
Different results were obtained in a study of the alkylation of an aromatic system, viz. phenylmercury bromide<sup>33</sup>. In contrast to ethyl esters of  $\alpha$ -bromomercuriphenylacetic acids, phenylmercury bromide does not form a complex with triphenylbromomethane under these conditions, and, therefore, alkylation reactions with both reagents,  $(C_6H_5)_3CBr$  and  $(C_6H_5)_3CBr \cdot HgBr_2$ , are of the second order, while as in the case of the mercuriated ester, the reaction rate decreases on going to the complex. However, the possibility that this is due to the presence of excess mercuric bromide cannot be ignored, since it has previously been shown<sup>34</sup> that mercuric bromide retards certain reactions of phenylmercury bromide, for example, protolysis. It may be presumed that the structure of the transition state is close to the non-cyclic structure in phenylmercury bromide reactions. This is confirmed by a study of the effect of structural factors. The effects of substituents in the phenylmercury bromide molecule on the reactions with triphenylbromomethane and its complex with mercuric bromide proved to be the same and characteristic of electrophilic substitutions. The assumption of a non-cyclic structure for the transition state in alkylation of phenylmercury bromide is also confirmed by the fact that in this case reaction also occurs under the influence of triphenylmethyl perchlorate. A rigorous kinetic study of the reaction is impossible, unfortunately, owing to the retarding effect of the mercuric bromide liberated. Thus, our results do not contradict the data reported in literature<sup>32</sup>, although the fact that the ethyl ester of  $\alpha$ -bromomercuriphenyl acetic acid and phenylmercury bromide behave differently naturally requires explanation.

The inhibiting effect of mercuric bromide in reactions of phenylmercury bromide is removed by the addition of an excess of tetrabutylammonium iodide to the reaction mixture. In this case, the reaction rate is sharply increased (by a factor of  $\sim 10^3$ ), which as shown previously<sup>34</sup>, is apparently associated with the formation of the complex  $[C_6H_5HgBrI^-]$ . This may be considered as an example of nucleophilic assistance. However, a further increase in iodide concentration with respect to concentrations of the reagents (on going from 1:10 to 1:20) leads to a slight, but appreciable decrease in the rate of the reaction. An analogous but more substantial decrease in reaction rate in two-anion catalysis (i.e., under conditions such

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that the formation of a complex with a charge of two is possible) has been observed recently in other reactions, and has been explained by hindrance to nucleophilic assistance by the nucleophilic portion of the molecule at the four-coordinated mercury. The slight effect observed in the present case apparently suggests that if nucleophilic coordination does exist, it is slight; however, its complete absence cannot be assumed.

Whether it is possible for an electrophilic substitution to occur in an organomercury compound depends on a number of factors. With respect to the molecule of the organomercury compound, one such factor is polarization of the Hg—C bond, i.e. primarily the presence of an effective positive charge on the mercury atom, which determines whether nucleophilic assistance is possible. A no less important factor is electronegativity of the radical at which the electrophilic attack is carried out. In the molecule of the attacking agent, another factor is the magnitude of the effective positive charge on the carbon atom and of the effective negative charge on the bromine atom. Data on the effect of substituents in the molecule of the attacking agent illustrate well the importance of both the nucleophilic attack on the mercury atom and the electrophilic attack on the carbon atom in alkylation reactions. On the one hand, tri(*p*-nitrophenyl)bromomethane, in which the C—Br bond is covalent so that nucleophilic assistance cannot occur, cannot generally be used as the alkylating agent (*p*-ethyl-, *p*-nitro-, and unsubstituted ethyl ethers of  $\alpha$ -bromomercuriphenylacetic acid, benzylmercury bromide, and *p*-



tolylmercury bromide do not react). On the other hand, a decrease in the electrophilicity of the alkylating agent leads to a decrease in the reaction rate, even under conditions such that there is some increase in nucleophilic coordination. Thus, the rate of the reaction with mercuriated esters decreases on going from triphenylbromomethane to the more ionized tri-*p*-tolylbromomethane.

Thus, the necessity of nucleophilic coordination is not the sole requirement in a number of cases. Apparently, an optimum situation is necessary: sufficient positive charge on the carbon atom constituting the electrophilic portion of the molecule and the possibility of nucleophilic assistance by the nucleophilic portion of the molecule. These requirements are not satisfied by either a covalent or a completely ionized compound, but only by a compound with a bond of a certain specific degree of ionic character.

Using the idea of the nucleophilic assistance it is possible to explain many peculiarities of S<sub>E</sub>-reactions. I will mention only some from these.

### The acceleration of isotope exchange reactions by means of bases

Some examples of reactions in which acceleration of isotope exchange by means of bases has been observed are given below.

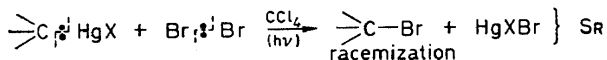
The reaction of organomercury compounds under the action of the



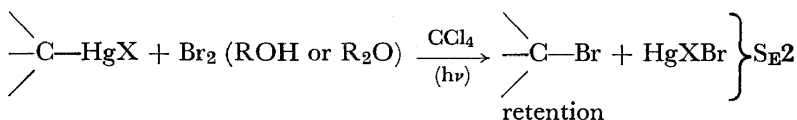
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The  $S_R \rightarrow S_E2$ -mechanism change in halodemercuration reactions under influence of ethers and alcohols

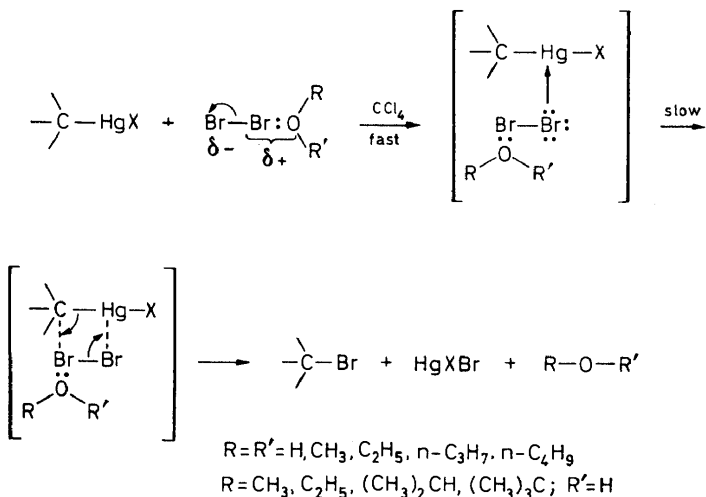
The bromodemercuration reaction in carbon tetrachloride solution in day light proceeds as a  $S_R$ -reaction with formation of racemic alkyl halide<sup>40</sup>



In the presence of ROH or R<sub>2</sub>O this reaction becomes S<sub>E</sub>2 and proceeds with strict retention of configuration<sup>41</sup>



Taking into consideration the hypothesis of nucleophilic assistance it is possible to explain this change of the mechanism because of more high ability of complexes like Br<sub>2</sub>·OR<sub>2</sub> to nucleophilic assistance compared to that of Br<sub>2</sub>:



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