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## Abstract

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## Chemistry

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# ON THE FOUR-MEMBERED TRANSITION STATE IN $S_E2$ REACTIONS AT A SATURATED CARBON ATOM

As a result of studying the kinetics and stereochemistry of electrophilic substitution reactions at a saturated carbon atom, we have come to the conclusion that, in nonpolar and slightly polar solvents, the indicated reactions proceed through a stage involving the formation of a cyclic four-membered transition state of type (A) ($^{1-3}$)*

$$-\mathrm{C}-\mathrm{HgX}+\mathrm{HgYZ}\longrightarrow(A)\longrightarrow-\mathrm{C}-\mathrm{HgZ}+\mathrm{HgXY}$$

I. $X = Y = \mathrm{Hal}; \quad Z = \mathrm{Alk};$
II. $X = \mathrm{Alk}; \quad Y = Z = \mathrm{Hal};$
III. $X = Y = Z = \mathrm{Hal};$
IV. $Z = \mathrm{Alk}; \quad X = Y = \mathrm{Hal};$
V. $X = Z = \mathrm{Alk}; \quad Y = \mathrm{Hal}.$

The grounds for accepting such a transition state are the following: the reactions are bimolecular (overall second kinetic order and first order with respect to each component), proceed with strict retention of the stereochemical configuration, i.e., the newly entering metal atom takes the place of the leaving one ($^{4,5}$); an open transition state of type (B) is unlikely in nonpolar and slightly polar solvents, since it would lead to the intermediate formation of the ions** $\mathrm{HgX}^+$ and $\mathrm{Y}^-$.

$$-\mathrm{C}-\mathrm{HgX}+\mathrm{HgYZ}\longrightarrow(B)\longrightarrow-\mathrm{C}-\mathrm{HgZ}+\{\mathrm{HgX}^+\ \mathrm{Y}^-\}\longrightarrow\mathrm{X}-\mathrm{Hg}-\mathrm{Y}$$

Naturally, in the case of solvents whose molecules contain atoms with unshared electron pairs (pyridine, dimethylformamide, ammonia), one or both Hg atoms in the transition state must be solvated or even linked by a coordination bond with solvent molecules (transition states ($A'$) and ($A''$)).

For reactions of monoalkyl isotope exchange (III) and symmetrization (I), we have proved such coordination experimentally. Thus, isotope exchange of the ethyl ester of $\alpha$-bromomercuriphenylacetic acid with bromomercury in dimethylformamide is in fact the reaction of RHgX and the complex $HgX_2$ with dimethylformamide ($^{8}$):

$$RHgX + {}^{*}HgX_2 \cdot DMFA \rightleftarrows R{-}{}^{*}HgX + HgX_2 \cdot DMFA.$$

* $S_E2$-reactions proceeding through the stage of a cyclic transition state are often denoted by the symbol $S_Ei$.

** The course of $S_E2$-reactions through transition state (B) is quite probable in polar solvents ($^{6,7}$).

Undoubtedly, when the reaction is carried out in pyridine ($^{9}$, $^{3}$), the active reagent is ${}^{*}HgX_2 \cdot C_5H_5N$, and not free ${}^{*}HgX_2$. The symmetrization reaction of this same substance under the action of ammonia in chloroform,

$$2RHgX + 2NH_3 \rightarrow R_2Hg + HgX_2 \cdot (NH_3)_2,$$

proceeds through a preliminary stage of formation of a complex of the organomercury compound with ammonia ($^{10-12}$), apparently according to scheme (I):

$$\begin{aligned} &a) \quad R{-}HgX + NH_3 \xrightleftharpoons{\text{rapid}} R{-}HgX \cdot NH_3, \\ &b) \quad 2R{-}HgX \cdot NH_3 \xrightarrow{\text{slow}} R_2Hg + HgX_2 \cdot (NH_3)_2 \; S_E2, \end{aligned} \tag{I}$$

The $S_E2$ reaction in this case proceeds through a transition state of type (A″). It should be noted that, following Whitmore' s scheme accepted in the literature ($^{13}$, $^{14}$) for the symmetrization of RHgX under the action of an excess of NaJ,

$$2RHgX \rightleftharpoons R_2Hg + HgX_2 \qquad HgX_2 \xrightarrow{NaJ} Na_2HgJ_4^{*},$$

we initially ($^{15}$) considered symmetrization under the action of ammonia as an analogous two-stage process (scheme II):

$$\begin{aligned} &a) \quad 2RHgX \rightleftharpoons R_2Hg + HgX_2, \\ &b) \quad HgX_2 + 2NH_3 \rightarrow HgX_2 \cdot (NH_3)_2. \end{aligned} \tag{II}$$

Here the first, slow, stage of the $S_E2$ reaction is a process proceeding through a transition state of type (A). At the same time, we constantly had in mind ($^{1-3}$) the possibility of a reaction according to scheme I, with initial formation of complexes of RHgX with $NH_3$.

Both schemes did not fully reflect all the features** of the rather complicated reaction under consideration; however, what they share is the main point—the fundamental similarity of the transition states (compare A and A″).

Recently (10–12) we came to the conclusion that scheme (I) better explains the experimental material accumulated by us up to that time. Thus, for example, the fact that the reaction goes to completion only when the ratio $NH_3 : RHgBr$ is not less than $10 : 1$ can be explained by the equilibrium (a) of scheme I being shifted strongly to the left. In addition, in studying the spectra of ethyl ether of $\alpha$-bromomercuriphenylacetic acid (and benzylmercury chloride) in chloroform solution in the presence of ammonia, and in studying the electrical conductivity of RHgX solutions in methanol in the presence of various amines (10, 12), we also obtained experimental data supporting scheme (I).

It is easy to see, however, that the general conclusions about the mechanism of $S_E2$ reactions at a saturated C atom, drawn both from consideration of transition state (A) without taking into account solvation or coordination of Hg atoms and from considering them, will be identical, since transition state (A″) differs in no fundamental way from transition state (A).

In connection with the foregoing, the article by Jensen that appeared in 1964 (17) cannot fail to surprise; in it he criticizes scheme (II) and declares the general theoretical conclusions on $S_E2$ reactions, which we drew from the experimental material of the symmetrization reaction, to be unfounded. Jensen rightly assumes that the reaction proceeds through the stage of preliminary formation of complexes of RHgX with $NH_3$ in accordance with scheme (I) or (III) (considering the latter more probable) *:

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* At the present time we have obtained (16) definite experimental evidence for the formation of $RHgX_2^-$ complexes. It may be thought that the Whitmore reaction proceeds through a stage of preliminary formation of complexes of this kind.

** Thus, for example, it was incomprehensible why additions of deliberately added $R_2Hg$ (obtained by symmetrization of RHgBr with ammonia) slow the reaction rate, whereas the rate of the symmetrization reaction remains constant despite the accumulation of its final substance $R_2Hg$ during the course of the reaction (15). As we have now established, such retardation is caused not by $R_2Hg$, but by negligible impurities in it, arising as a result of partial decomposition during crystallization of $R_2Hg$ obtained under the action of ammonia. By symmetrizing the organomercury salt with triphenylphosphine, we obtained $R_2Hg$ that was considerably more easily purified. Additions of $R_2Hg$ obtained in this way do not affect the rate of symmetrization.

$$\begin{aligned} &\text{a) } RHgX + 2NH_3 \underset{\text{slow}}{\overset{\text{fast}}{\rightleftarrows}} RHgX\cdot(NH_3)_2, \\ &\text{b) } RHgX\cdot(NH_3)_2 + RHgX \rightleftarrows R_2Hg + HgX_2\cdot(NH_3)_2. \end{aligned} \qquad \text{(III)}$$

This point of view coincides with ours, formulated before publication of Jensen's article (it is quite natural that Jensen, with works (10-12) still unknown to him, should have been unaware of this). It is difficult to believe, however, that Jensen really does not understand that the question he discusses is a particular one and is completely nonessential in the general front of our work, and that the general conclusions on the mechanism of $S_E2$ reactions (retention of the stereochemical configuration (4), the influence of structural factors (1, 24), compare also (20), of the nature of the solvent and of polar additives (1), the interpretation of the phenomenon of "cosymmetrization" (21)) should be the same regardless of whether we adopt the transition state (A) "in the pure form," abstracting from solvation or coordination of mercury atoms (scheme II), or the transition state (A″) (scheme I), or, finally, the transition state (A‴), in which one mercury atom is coordinated with two ammonia molecules and the second is not coordinated at all (scheme III).

The principal feature of all these transition states is the four-membered ring (A). It is this that relates the symmetrization reaction *** to reactions II–V, and it is this that accounts for the coinciding theoretical conclusions made on the basis of independent study of $S_E2$ reactions of all five types.

In studying the influence of structural factors on the rate of the symmetrization reaction of a series of substituted ethyl esters of $\alpha$-bromomercuriphenylacetic acid, the conclusion was drawn that in the transition state (A) rupture of the old C–Hg bond plays a more important role than formation of the new one. The values of the second-order rate constants $K_2$ (ml/mol • sec) are as follows:

| $Y$ | *n*-$NO_2$* | *n*-J | *n*-Br | *m*-Br | *o*-Br | *n*-Cl | *n*-F | H | *n*-$CH_3$ | *m*-$CH_3$ | *o*-$CH_3$ | *n*-$C_2H_5$ | *n*-$(CH_3)_2CH$ | *n*-$(CH_3)_3C$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $K$ | 17 730 | 670 | 540 | 1445 | 426 | 470 | 148 | 110 | 34 | 71 | 32 | 41 | 42 | 28 |

(A)

* The constant $K_2$ was calculated from the condition of applicability of the Hammett equation ($\rho = 2.85$).

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* At present there are no experimental grounds for choosing between schemes (I) and (III). It is not impossible, even, that both reaction paths are realized.

** In Jensen’s article there is essentially no experimental part, with the exception of two crude experiments. The first, a visual experiment—the action of ammonia on mercuric bromide in chloroform—was performed in order to show that this reaction is fairly fast (no one asserted the contrary). The second experiment—precipitation of a deposit (of unknown composition) when ammonia is passed through a chloroform solution of secondary $C_4H_9HgBr$—was performed in order to prove the fundamental possibility of formation of complexes of organomercury salts with ammonia. This experiment is more than superfluous, since in principle the formation of complexes with ammonia and amines has been described in the literature (18, 19) (apparently these works escaped Jensen’ s attention).

What is needed is something else—the study of complexes with ammonia (or amines) specifically of those model substances (ethyl esters of $\alpha$-bromomercuriarylacetic acids) on the example of which we studied the symmetrization reaction. Such a study was carried out by us (12) and is being continued at the present time.

*** In the following, when discussing the characteristic features of the symmetrization reaction, we shall, for clarity, continue to consider the four-membered cyclic transition state (A), so to speak “in the pure form,” bearing in mind, of course, that in reality either one or both Hg atoms are coordinated by ammonia molecules.

As can be seen, the order of influence of the substituents proves to be reversed in comparison with typical $S_E2$ reactions. This circumstance may be interpreted as meaning that, owing to the specific character of our organomercury objects (the high lability of the C—Hg bond), the $S_E2$ reaction under study lies in a borderline region, close to the region of $S_E1$ reactions, which until recently were unknown.*

Since in the transition state (A) not only the old C—Hg bond is being broken, but also the old Hg—Br bond, it is natural to assume that this kind of transition state will be attained more readily in the case of a reaction between different molecules (Ia) and (IIa):

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

$$\longrightarrow \text{ (B) } \longrightarrow YC_6H_4CH(HgCHXC_6H_4)COOR + HgBr_2 \cdot (NH_3)_2$$

Experiment fully confirmed this assumption (21). Finally, using radioactive mercury $Hg^{203}$, we proved that the Hg atom from the starting molecule (Ia) with the electronegative substituent Y passes preferentially into the complex $HgBr_2 \cdot (NH_3)_2$, while the Hg atom from molecule (IIa) with substituent X passes into the final organomercury compound, as can also be predicted from transition state (B).

Thus, the cyclic transition state proposed by us in $S_E2$ reactions of organomercury compounds may at present be regarded as sufficiently well substantiated.**

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* Proceeding from this assumption, we were the first to succeed in carrying out the $S_E1$ mechanism ($^{22}$), using as an example the reaction of isotope exchange of ethyl $\alpha$-bromomercuriphenylacetate with bromine mercury in dimethyl sulfoxide.

** Ingold and coworkers ($^{25}$), who in recent years have also been studying $S_E$ reactions of organomercury compounds, develop ideas fundamentally close to ours.

*Note: Figure translations are in progress. See original paper for figures.*

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