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**Abstract**

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### CHEMISTRY

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# ON THE QUESTION OF THE MECHANISM OF BIMOLECULAR ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

On the basis of a study of the kinetics and stereochemistry of electrophilic-substitution reactions at a saturated carbon atom (1)–(5):

$$2R_1R_2R_3CHgX \rightarrow (R_1R_2R_3C)_2Hg + HgX_2, \quad (1)$$

$$R_1R_2R_3CHgX + Hg^{203}X_2 \rightleftarrows R_1R_2R_3CHg^{203}X + HgX_2, \quad (2)$$

$$R_1R_1R_3CHgX + RHg^{203}X \rightleftarrows R_1R_2R_3CHg^{203}X + RHgX, \quad (3)$$

$$(R_1R_2R_3C)_2Hg + HgX_2 \rightarrow 2R_1R_2R_3CHgX, \quad (4)$$

$$(R_1R_2R_3C)_2Hg + R_1R_2R_3CHg^{203}X \rightleftarrows (R_1R_2R_3C)_2Hg^{203} + R_1R_2R_3CHgX \quad (5)$$

one of us (1-4) put forward the view that all these reactions have similar mechanisms, which may be represented by the following scheme:

$$R_1R_2R_3C{-}HgX + Hg{-}R \rightleftarrows \left[\begin{array}{c} R_1 \\ R_2{-}C \\ R_3 \end{array} \cdots Hg \cdots Hg\right] \rightleftarrows R_1R_2R_3C{-}Hg{-}R + HgX$$

(Reaction (1): R = $R_1R_2R_3C$, Y = X-halide; reaction (2): R = Y = X-halide; reaction (3): Y = X-halide; reaction (4): X = $R_1R_2R_3C$, R = Y-halide; reaction (5): R = X = $R_1R_2R_3C$, Y-halide.)

The assumption that, in all the cases under consideration, bimolecular electrophilic-substitution reactions proceed through one and the same cyclic four-membered transition state (A) was made on the basis of the following experimental facts. All the reactions are bimolecular (first order with respect to each of the reacting components) and proceed with retention of configuration, i.e., the new metal atom enters at the place of the departing one; finally, these reactions proceed in nonpolar and slightly polar solvents, i.e., under conditions in which the intermediate existence of ions is highly improbable*. Similar ideas concerning the mechanism of $S_E2$ reactions are being developed by Ingold and co-workers (5-10).

The American chemist Dessy proposed a fundamentally different mechanism for bimolecular electrophilic-substitution reactions of the type under consideration (11). Dessy studied the reaction of phenylethylmercury with labeled sulema,

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* It should, of course, be borne in mind that, when the reactions under consideration are carried out in increasingly polar solvents, the probability should increase that $S_E2$ reactions proceed through a noncyclic transition state with intermediate formation of solvated ions, for example: (12, 6)

$$> CHgCl + Hg^*Cl_2 \rightleftarrows [> C \cdots Hg \cdots Hg] \rightleftarrows > CHg^*Cl + (ClHg^+Cl^-) \downarrow HgCl_2$$

$Hg^{203}$. According to his data, the radioactivity of sublimate is statistically distributed between the reaction products—phenylmercury chloride and ethylmercury chloride:

$$C_6H_5HgC_2H_5 + Hg^{203}Cl_2 \rightarrow C_6H_5Hg^{203}Cl\ (50\%) + ClHg^{203}C_2H_5\ (50\%).$$

On the basis of this result, Dessy proposed two possible mechanisms for the reaction under consideration:

(I) (II)

six-center transition state with Hg, $Hg^*$, Cl, Cl, $C_2H_5$, $C_6H_5$ four-membered transition state: Cl—Hg

The first mechanism is associated with the formation of a six-center spatial transition state (I); the second mechanism (which Dessy considers more probable)

consists in the formation of a four-membered transition state (II), in which each of the mercury atoms is bonded simultaneously to a chlorine atom, a phenyl group, and an ethyl group.

The mechanisms proposed by Dessy seemed so improbable to us that we repeated Dessy' s work, studying not only the reaction of ethylphenylmercury with radioactive sublimate, but also with radioactive mercury bromide. As we expected, Dessy' s work proved to be erroneous*. In all cases the radioactivity from the mercury halide passes only into phenylmercury halide:

$$C_2H_5HgC_6H_5 \begin{cases} \xrightarrow{Hg^{203}Cl_2} C_2H_5HgCl + ClHg^{203}C_6H_5 \\ \xrightarrow{Hg^{203}Br_2} C_2H_5HgBr + BrHg^{203}C_6H_5 \end{cases}$$

Thus, there are no experimental data for assuming transition states in $S_E2$-reactions at a saturated carbon atom that are more complex than those proposed by us and by Ingold et al.

## Experimental Part**

**Preparation of phenylethylmercury.** Phenylethylmercury was obtained from 0.10 mole of $C_2H_5HgBr$ and 0.11 mole of phenyllithium and distilled in vacuo at 5 mm Hg in the range 105—108°.

| | | | |
|---|---|---|---|
| Found, %: | C 31.81; 31.99; | H 3.28; 3.32; | Hg 64.35; 64.01. |
| $C_8H_{10}Hg$. Calculated, %: | C 31.32; | H 3.29; | Hg 65.39. |

The increased carbon content and decreased mercury content are explained by an admixture of biphenyl (about 3%). An experiment with a sample containing about 6% biphenyl showed that small amounts of this impurity do not affect the result of the reaction of the substance with mercury bromide. Decomposition with hydrochloric acid was used as the criterion of purity of phenylethylmercury. To 0.19 g of phenylethylmercury in 1 ml of absolute alcohol, 0.2 ml of concentrated hydrochloric acid was added; after 5 min the mixture was diluted with water, the precipitate was separated and washed with 1 ml of ether; yield of $C_2H_5HgCl$ 0.162 g (~ 95%), m.p. 193—194° (literature data 190—193 ([13])).

**Reaction of phenylethylmercury with $Hg^{203}Br_2$.** Two experiments were carried out with different conditions for isolating the reaction products. In one of them we were able to separate phenylmercury bromide and ethylmercury bromide and to determine the activity of both products. In the other experiment, the separation of the products was performed under conditions close to those of Dessy' s experiment. In this case, isolation of ethylmercury bromide in pure

form is difficult; therefore, only the activity of phenylmercury bromide was determined.

* Apparently, Dessy, despite the blank experiments performed, did not succeed in avoiding secondary isotope exchange.

** The experimental part was carried out with the participation of V. N. Nikol'skii.

1. A solution of 0.838 g (2.73 mmole) of phenylethylmercury in a minimal amount of absolute alcohol was mixed in the cold with a solution of 0.985 g (2.73 mmole) of labeled mercuric bromide in alcohol; the precipitate that separated was filtered off and washed with hot water and alcohol. Ethylmercury bromide was steam-distilled over 3 hours and recrystallized twice from alcohol, mp 193–194° (literature data 193.5° (14)). The phenylmercury bromide remaining in the distillation flask was recrystallized from xylene, mp 272–273° (literature data 275° (15)). The activity of samples of both organomercury compounds and of the initial mercuric bromide was determined on an MS-4 $\gamma$-counter; distribution of activity: in $C_6H_5HgBr$ 95%, in $C_2H_5HgBr$ 1.7%.

2. 0.440 g (1.43 mmole) of phenylethylmercury in a minimal amount of absolute alcohol was mixed in the cold with a solution of 0.517 g (1.43 mmole) of labeled mercuric bromide in alcohol. The precipitate was washed with alcohol and heated with 40 ml of absolute methanol to boiling for 15 min. The solution was filtered, cooled, and the crystals that separated were filtered off, washed with alcohol and ether, and recrystallized twice from absolute alcohol. The mp of the phenylmercuric bromide obtained was 273°. The activity of the sample was determined on an MS-4 $\gamma$-counter for liquids (see below); the mean result of the activity determination in phenylmercury bromide was 92.0%.

**Reaction of phenylethylmercury with $Hg^{203}Cl_2$.** To 0.135 g (0.44 mmole) of phenylethylmercury in 2 ml of absolute methanol was added 0.120 g (0.44 mmole) of labeled sublimate in 3 ml of absolute methanol. The precipitate that formed was heated with 15 ml of absolute methanol for 20 min, during which the entire precipitate went into solution. The latter was filtered hot, and the crystals that separated on cooling were recrystallized from absolute methanol. The phenylmercury chloride obtained had mp 249° (literature data 250° (16)). Results of determination of the activity of phenylmercury chloride on a $\gamma$-counter for liquids for different weighed portions: 95–98% (the activity of the initial mercuric halide was in all cases taken as 100%).

**Activity measurements.** Mercuric bromide labeled with $Hg^{203}$ was prepared from metallic mercury and recrystallized twice from water and from alcohol. Sublimate labeled with $Hg^{203}$ was prepared from mercuric bromide via mercuric oxide and recrystallized in the same way.

The activity of the samples was measured either on an MS-4 $\gamma$-counter or on an

MS-4 $\gamma$-counter for liquids. In the first case the activity was determined by the "accumulation" method; in the second case the samples for determinations were prepared as follows: a weighed portion of the substance under study, about 5.00-8.00 mg, was dissolved in 20.0 ml of dioxane and placed in a standard cuvette. The accuracy of determination in all cases was about 5%.

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