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Abstract

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Kinetics of the Reaction of Electrophilic Substitution at a Saturated Carbon Atom

(Presented by Academician A. N. Nesmeyanov, 15 III 1957)

A. N. Nesmeyanov, S. S. Poddubnyi, and one of us (^{1}), using as an example the diastereomeric *l*-menthyl esters of α-bromomercuriphenylacetic acid, established that symmetrization of organomercury salts with ammonia

$$R_1R_2R_3C—|HgX + R_1R_2R_3C—Hg|—X \xrightarrow{NH_3} (R_1R_2R_3C)_2Hg$$

$$(R_1 = C_6H_5; \quad R_2 = H; \quad R_3 = COOC_{10}H_{19}),$$

which is a reaction of electrophilic substitution at a saturated carbon atom, proceeds with retention of the stereochemical configuration. The same results were later obtained by Cram (^{2})*, and also by Winstein and co-workers (^{3}), in the study of other reactions of electrophilic substitution at a saturated carbon atom.

Hughes and Ingold, on the basis of analogy with the S_N1—S_N2 mechanisms of nucleophilic substitution, proposed (^{4}) that, in the case of electrophilic substitution, retention of configuration would occur by the S_E1 mechanism, and inversion by the S_E2 mechanism.

It seemed to us, however, a priori unlikely that the symmetrization reaction of α-bromomercuriphenylacetic esters would proceed through the stage of formation of an anion (see formula I) as a kinetically independent particle (S_E1 mechanism), since in such a case one would expect not retention of configuration at the carbon atom, but racemization as a consequence of conjugation of the free electron pair with the π-electrons of the carbonyl group. In this connection, we undertook a study of the kinetics of the reaction under consideration.

$$C_6H_5—\ddot{C}H—C(=O)OR \qquad I$$

The study of the kinetics of the symmetrization reaction was carried out with the ethyl and *l*-menthyl esters of α-bromomercuriphenylacetic acid; in the case of

Fig. 1

Figure 1: Fig. 1

the *l*-menthyl ester, the reaction kinetics was studied using a mixture of diastereomers and one of the diastereomers with m.p. 156° (from alcohol), $[\alpha]_D^{18} = -90°$; $C = 0.58972$; $l = 1.9$; $\alpha = -1°$.

To study the reaction order with respect to the starting substance $R_1R_2R_3C—HgX$, we used a method based on the principle of nephelometry. The photocell recorded the change in the amount of transmitted light during the course of the reaction as a result of precipitation of the $(NH_3)_2 \cdot HgBr_2$ precipitate according to the equation:

$$2R_1R_2R_3C—HgBr + 2NH_3 \rightarrow (R_1R_2R_3C)_2Hg + HgBr_2 \cdot (NH_3)_2$$

$$(R_1 = C_6H_5; \quad R_2 = H; \quad R_3 = COOC_2H_5 \text{ or } COOC_{10}H_{19}).$$

The experiments were carried out at one and the same intensity of the light source.

The reaction was conducted in absolute chloroform with dry ammonia at room temperature. It was carried out at high dilutions, which prevented aggregation of the precipitate formed. It was additionally verified that the precipitated solid did not contain starting or final products. Weigh— of the precipitate formed at the moment the reaction ended for substance concentrations of $6.8 \cdot 10^{-5}$ and $3.4 \cdot 10^{-5}$ mole/ml and an ammonia concentration of $1 \cdot 10^{-3}$ mole/ml, it was established that its amount corresponds to the stoichiometric amount and, consequently, the reaction goes to completion. At smaller amounts of ammonia the reaction does not go to completion.

For both mercurated esters (ethyl and menthyl), the reaction is of second order with respect to the substance; this order is calculated both from the initial concentrations C of the substance under study and from the course of the kinetic curve. Symmetrization of the menthyl ester proceeds at a lower rate than that of the ethyl ester.

Fig. 1

The reaction was carried out at different concentrations of the ethyl ester of α-bromomercuriphenylacetic acid. $C_0 \cdot 10^5$ mole/ml: 6.8; 6.12; 5.44; 4.76; 4.08; 3.40; 2.72; 1.70; 1.36; 0.85 and an ammonia concentration of $1 \cdot 10^{-3}$ mole/ml. Fig. 1 gives the curves $I = f(t)$, where I is the amount of light passing through

* In a number of reactions studied by him, Cram also observed inversion of configuration.

Fig. 2

Figure 2: Fig. 2

the system. Under these conditions the reaction goes to completion; therefore we were able to calibrate the curves $I = f(t)$ according to concentrations, taking into account that, for the same amount of transmitted light, the amount of precipitate formed is also the same. This allowed us to calculate the reaction rate constant, which is the constant of a second-order reaction.

$$K_2 = \frac{1}{C_0 t}\left(\frac{C_0}{C} - 1\right).$$

C is the concentration of the substance at time t; $K_2 = K'(\mathrm{NH_3})^2$, as will be shown below.

Table 1 gives the initial concentrations of the substance, the corresponding half-life periods, and the values of the reaction rate constant.

Table 1

$C_0 \cdot 10^5$, mole/ml	6.80	5.44	3.40	2.72	1.70
$\tau_{1/2}$, sec	136	190	305	400	400
k_2, ml/mole· sec	110	100	100	90	140
K_{av}	~ 110	~ 110	~ 110	~ 110	~ 110

Fig. 2

The second part of the work was to establish the order of the reaction with respect to the second component—ammonia.

The method of determining the reaction order by changing the initial concentration of one of the components proved unsuitable for determining the reaction order with respect to ammonia, since the ammonia concentration can be varied only in the direction of decreasing it because of the poor solubility of the starting substance in chloroform. At lower ammonia concentrations, however, the reaction does not go to completion. Moreover, the concentration of precipitate under these conditions (when the ammonia concentration is smaller than the concentration of the substance) is below that corresponding to the coagulation threshold.

In determining the order with respect to ammonia, first, the stoichiometric amount of ammonia consumed in the reaction was determined from the drop

Fig. 3

Figure 3: Fig. 3

in its pressure before and after the reaction. It was shown that 1 mole of ammonia is consumed per 1 mole of substance. Second, the rate of consumption of ammonia during the reaction was measured at different initial concentrations of ammonia and at a definite initial concentration of the substance; in doing so we used the following procedure: ammonia was introduced into an evacuated reaction vessel under a definite pressure, after which the substance in chloroform was added. The reaction was stopped by adding an excess of HCl*, which was then titrated. The reaction went to completion over several days. The initial amounts taken were: substance, $1.36 \cdot 10^{-3}$ mole; ammonia, C_0, $(3.28;\ 2.76;\ 2.12;\ 1.60;\ 1.07) \cdot 10^{-3}$ mole.

Table 2

$C \cdot 10^3$, mole	3.28	2.76	2.12	1.60	1.07
$C^2 \cdot 10^6$, mole	10.75	7.62	4.49	2.56	1.14
$v_{0.5}$*	0.31	0.24	0.15	0.09	0.04

* $v_{0.5}$ is the amount of starting substance, in moles, that reacted in 0.5 hour.

If the change in ammonia concentration over the first 0.5 hour is taken as the initial rate of the reaction (which is possible with sufficient accuracy, since the reaction is completed over several days), it is easy to see that the initial rate of ammonia consumption is directly proportional to the square of its initial concentration (Table 2, Fig. 2). Thus, the symmetrization reaction of organomercury salts under the action of ammonia studied by us is second order with respect to the substance and second order with respect to ammonia.

Fig. 3

In the case where the experiments were carried out at various concentrations of ammonia, less than $1.0 \cdot 10^{-3}$ mole/ml but always exceeding the concentration of the organomercury substance, the reaction proceeded not only at different rates but also to different extents. Figure 3 gives curves $I = f(t)$ for a concentration of the substance of $6.8 \cdot 10^{-5}$ mole/ml and ammonia concentrations C_0: $(6.35;\ 5.02;\ 3.27;\ 1.75) \cdot 10^{-4}$ mole/ml. The reaction terminates at different amounts of substance consumed.

These data make it possible to suppose that the symmetrization reaction under consideration is reversible.**

Confirmation of the presence of reversibility is provided by studying the effect of additions of the symmetrical product $(R_1R_2R_3C)_2Hg$, formed in the course of the reaction. The reaction was carried out at an initial concentration of the substance of $6.8 \cdot 10^{-5}$ mole/ml, ammonia $1 \cdot 10^{-3}$ mole/ml, and additive concentrations C, $(0.48;\ 0.96;\ 1.92)\cdot 10^{-5}$ mole/ml. It was found that additions of the final product slow the rate reaction. In Fig. 4 the curves $I = f(t)$ are given, illustrating this influence.

The data obtained by us for the symmetrization of organomercury salts under the action of ammonia make it possible to propose the following two-stage reaction mechanism:

$$\text{I}:\quad 2\mathrm{R_1R_2R_3C{-}HgBr} \rightleftharpoons [\mathrm{R_1R_2R_3C}\cdots\mathrm{HgBr}\cdots\mathrm{CR_1R_2R_3}] \rightleftharpoons (\mathrm{R_1R_2R_3C})_2\mathrm{Hg} + \mathrm{HgBr_2} \quad S_{\mathrm{E}}2$$

$$\text{II}:\quad \mathrm{HgBr_2} + 2\mathrm{NH_3} \rightleftharpoons \mathrm{HgBr_2(NH_3)_2}$$

Stage I (reversible) is a reaction of electrophilic substitution at a saturated carbon atom. In stage II*** ammonia binds $\mathrm{HgBr_2}$ and shifts equilibrium I to the right.

Fig. 4

The results of the study of the stereochemistry and kinetics of the symmetrization of organomercury salts allow us for the first time to establish a bimolecular mechanism ($S2$) for an electrophilic substitution reaction at a carbon atom, proceeding with retention of stereochemical configuration.

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named after M. V. Lomonosov

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* The dilute HCl used (0.149 N) reacts neither with the starting nor with the final organomercury compounds.

** Similar results are reported by Whitmore for the symmetrization reaction of organomercury compounds with potassium iodide (^{5}).

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* From the fact of the existence of equilibrium I it follows that not only the symmetrization reaction, but also the reverse reaction

$$(R_1R_2R_3C)_2Hg + HgBr_2 \rightarrow 2R_1R_2R_3C{-}HgBr,$$

which is likewise a process of electrophilic substitution at a saturated carbon atom, must also apparently proceed with retention of stereochemical configuration. Indeed, contrary to our initial opinion (1), the reaction of the menthyl ester of α-mercuri-bis-phenylacetic acid with $HgBr_2$ in acetone in the cold, as shown by us together with J. I. Freidlina, proceeds with retention of configuration. The racemization observed during this reaction at 56° is due to secondary processes.

** The composition of the bromomercury complex formed with ammonia, according to our data and the data of a number of other authors (6), may vary depending on the reaction conditions.

*** Stage II of the symmetrization reaction is also apparently reversible, since the depth of conversion of the starting substance depends substantially on the amount of excess ammonia.

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

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