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Abstract

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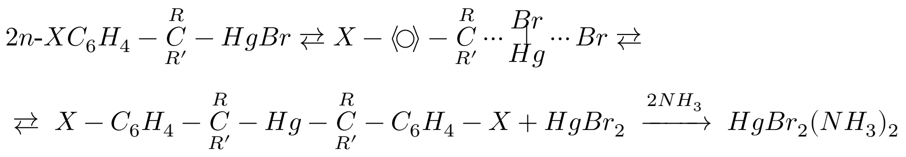
THE "COSYMMETRIZATION" REACTION OF ORGANOMERCURY SALTS

It was shown earlier (1) that the symmetrization reaction of ethyl esters of α-bromomercuriacetic acids under the action of ammonia in abs. chloroform is an electrophilic bimolecular substitution at a saturated carbon atom, for which a mechanism was proposed that includes a cyclic transition state



$$2n\text{-}XC_6H_4-\overset{R}{\underset{R'}{C}}-HgBr \rightleftarrows X-\langle\bigcirc\rangle-\overset{R}{\underset{R'}{C}}\cdots\overset{Br}{\underset{Hg}{|}}\cdots Br \rightleftarrows$$

$$\rightleftarrows X-C_6H_4-\overset{R}{\underset{R'}{C}}-Hg-\overset{R}{\underset{R'}{C}}-C_6H_4-X+HgBr_2 \xrightarrow{2NH_3} HgBr_2(NH_3)_2$$

A study of the influence of the nature of substituents X, located in the para position of the benzene ring, on the reaction rate showed that electron-acceptor substituents accelerate, whereas electron-donor substituents retard, the process*. The influence of substituents satisfies the Hammett equation (2).

It is natural to suppose that, when ammonia acts on a mixture of two organomercury salts $R—Hg—Br$ and $R'—Hg—Br$, three reactions may proceed simultaneously.

$$2RHgBr \to R_2Hg, \tag{a}$$
$$2R'HgBr \to R_2'Hg, \tag{b}$$
$$RHgBr + R'HgBr \to R—Hg—R'. \tag{c}$$

Since in the four-membered transition state (A) not only the $C—Hg$ bond but also the $Hg—Br$ bond is broken, one may expect that the reaction will be facilitated in the case of "cosymmetrization" of such disubstituted esters: $XC_6H_4CH(HgBr)CO_2C_2H_5$ and $YC_6H_4CH(HgBr)CO_2C_2H_5$, in which substituents X and Y exert sharply different polar effects. If, for example, substituent X is an electron-acceptor and substituent Y is an electron-donor group, then the former will facilitate cleavage of the old $C—Hg$ bond, and the latter, that of the $HgBr$ bond

(A)

“Cosymmetrization” was studied for such pairs of mercurated esters of the type $XC_6H_4CH(HgBr)CO_2C_2H_5$ and $YC_6H_4CH(HgBr)CO_2C_2H_5$, where 1) $X = Br,\ Y = H$; 2) $X = H,\ Y = CH_3$; 3) $X = Br,\ Y = CH_3$.

* This character of the influence of substituents apparently indicates that, in this reaction (although it is bimolecular), the decisive importance lies in cleavage of the old C—Hg bond, and not in formation of the new one.

The kinetics of the “cosymmetrization” reaction was studied, as before, by the nephelometric method (^{3}). At the same time, the kinetic dependence $I = f(t)$ was studied for each of the components at the same initial concentrations as in the “cosymmetrization” reaction.

From the curves $I = f(t)$, with the aid of the calibration curve $I = f(C_0 - C)$, kinetic curves $C_0 - C = f(t)$ were obtained, where I is the intensity of the light passing through the system, C_0 is the initial concentration, and C is the current concentration of the reagents. From the curves $C_0 - C = f(t)$, the rate constants of the second-order reaction and the initial reaction rates (v_0) were found; for the latter the amount of product that reacted in the first 30 sec was taken, as well as the relative reaction rates (w). The data obtained are summarized in Table 1 (the calculation was made in relative units; the concentration $C_0 = 6.8 \cdot 10^{-5}$ mole/ml was taken as 1).

As is seen from the data of Table 1, the initial rates of the “cosymmetrization” process are greater than the sum of the initial reaction rates for each of the components, taken at the same concentrations, by the amount Δv_0, which may be called the “cosymmetrization” effect. Such an excess in rate is especially large for the substituents most different in polarity (methyl and

Table 1

	1	2	3	4	5	6	7	8	9
v_0	0,055	0,025	0,17	0,145	0,08	0,32	0,225	0,37	0,145
Δv_0				0,065		0,095		0,175	
$\frac{v_{\mathrm{OX,Y}}}{v_{\mathrm{OX+Y}}}$				1,8		1,4		1,4	
k_2, ml/mole·sec	140	45	540	91		242		297	
w	140	45	540	91	46	242	170	297	146

I. 1 –H–R–Hg–R–H; 2 –CN$_3$–R–Hg–R–CH$_3$; 3 –Br–R–Hg–R–Br; 4 –H –R–Hg–R–CH$_3$, H–R–Hg–R–H, CH$_3$–R–Hg–R–CH$_3$; 5 –H–R–Hg–R–H, CH$_3$–R–Hg–R–CH$_3$; 6 –H–R–Hg–R–Br, H–R–Hg–R–H, Br–R–Hg–R–Br;

7 –H–R–Hg–R–H, Br–R–Hg–R–Br; 8 –Br–R–Hg–R–CH_3, Br–R–Hg–R –Br, CH_3–R–Hg–R–CH_3; 9 –Br–R–Hg–R–Br, CH_3–R–Hg–R–CH_3, R = –C_6H_4–CH–$CO_2C_2H_5$.

II. Δv_0 is the difference between the initial rate of the "cosymmetrization" reaction and the sum of the initial rates of the components at the same concentrations; $v_{\mathrm{OX,Y}}/v_{\mathrm{OX+Y}}$ is the ratio of the initial rate of the "cosymmetrization" reaction to the sum of the initial rates of the components at the same concentrations.

bromine), which agrees with the proposed transition state (A). The presence in the reaction mixture of an unsymmetrical, fully substituted organomercury compound $R—Hg—R'$ was shown by refractometric measurements on an ITR-1 interferometer.

Table 2*

	1	2	3	4	5	6	7	8	9
m	5,30	5,60	6,46	10,75	10,90	12,66	11,70	14,84	12,00

* The compound numbers are the same as in Table 1.

Table 2 gives the shifts of the interference bands, with which the refractive indices are related by the following formula: $\Delta n = m\lambda/L$, where Δn is the difference in refractive indices, λ is the wavelength, and 2 is the length of the cuvette. For this purpose, on the one hand, the magnitudes of the shifts m caused by symmetrical organomercury compounds X–R–Hg–R–X and Y–R–Hg–R–Y at concentrations of $1.7 \cdot 10^{-5}$ mole/ml were determined, as well as the shifts caused by their mechanical mixture at a concentration of $3.4 \cdot 10^{-5}$ mole/ml (i.e., a mixture of two solutions, each of which was obtained as a result of the symmetrization of an individual component). On the other hand, the shift caused by the reaction mixture after cosymmetri-

in a concentration of $3.4 \cdot 10^{-5}$ mole/ml (with equimolecular ratios of the components). The measurements were carried out at a temperature of 19.5°.

From the data of Table 2 it is seen that the magnitude of the shift caused by a mechanical mixture of products in accordance with the additivity rule (4) is equal to the sum of the shifts caused by each product, but differs from the shift caused by the reaction mixture after "cosymmetrization."

According to transition state (A), in the "cosymmetrization" reaction the mercuric bromide formed must contain that mercury atom which belonged to the molecule $XC_6H_4CH(HgBr)CO_2C_2H_5$, having the more electronegative substituent. This assumption was tested using radioactive mercury Hg^{203}. The "cosymmetrization" of n-$BrC_6H_4CH(Hg^{203}Br)CO_2C_2H_5$* and n-$CH_3C_6H_4CH(HgBr)CO_2C_2H_5$ was studied at concentrations of $1.74 \cdot 10^{-5}$ mole/ml.

The activity was measured on a B-2 apparatus (MS-4 counter). The initial activity of the solution, which was 11731 counts/min, after symmetrization fell to 2100 counts/min. The activity of 0.01 g of precipitate was 660 counts/min, which for the entire precipitate amounted to 9055 counts/min (weight of the $HgBr_2 \cdot 2NH_3$ precipitate = 0.1372 g). The sum of these activities gives good agreement with the initial activity.

Thus, the principal activity passed into the $HgBr_2 \cdot 2NH_3$ precipitate. The presence of activity in the precipitate can only be the result of rupture of the carbon-mercury bond in the ethyl ester of α-bromomercuri-n-bromophenylacetic acid. This means that the reaction proceeds according to the scheme

$$n\text{-}CH_3C_6H_4CH(HgBr)COOC_2H_5 + n\text{-}BrC_6H_4CH(HgBr)COOC_2H_5 \rightleftarrows$$

[[structural formula: cyclic transition state containing BrC_6H_4, CH, Hg^{203}, Hg, $CO_2C_2H_5$, and C_6H_4CH

After completion of the reaction, 18% of the initial radioactivity remained in the solution.** This may be, on the one hand, a consequence of the parallel occurrence of symmetrization reactions of types (a) and (b) between like molecules of organomercury salts. On the other hand, it is not excluded that the reaction proceeds to a small extent through a transition state of the type

[[structural formula: transition state with two aromatic rings bearing substituents Y and X, $CH(CO_2C_2H_5)$

which is clearly less favorable energetically, but can occur with a certain probability.

Finally, it is quite probable that an isotope-exchange reaction proceeds to a small extent between the unsymmetrical fully substituted compound $R—Hg—R'$ and the radioactive organomercury salt. This type of isotope exchange is known (5).

* This compound was obtained by exchange of $n\text{-}BrC_6H_4CH(HgBr)CO_2C_2H_5$ with mercuric bromide labeled with Hg^{203}, in acetone.

** Blank experiments showed that no exchange occurs between the precipitated mercuric bromide ammoniate and the solution.

However, regardless of the reasons for the presence of 18% radioactivity in the solution, the main result of the experiment is beyond doubt: in the "cosymmetrization" reaction, it is predominantly the mercury atom from the molecule of the organomercury salt containing the less electronegative substituent that passes into the molecule of the symmetrical compound. Similar results were obtained in the "cosymmetrization" of another pair of mercurated esters, *n*-iso-$C_3H_7C_6H_4CH(Hg^{203}Br)CO_2C_2H_5$ with *n*-$BrC_6H_4CH(HgBr)CO_2C_2H_5$, but with the label in the compound bearing the electron-donor substituent.

As expected, the principal activity (70.5%) in this case remained in solution. Thus, the nature of the cleavage of the C—Hg and Hg—Br bonds in the transition state, depending on the electronic character of the substituents X and Y, may be regarded as confirmed*.

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* It is of interest to note that benzylmercury bromide, which itself is not symmetrized by ammonia, enters into the cosymmetrization reaction with ethyl esters of *n*-substituted α-bromomercuriphenylacetic acids.

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

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