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Abstract

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Isotopic Exchange of Certain Organomercury Salts with Metallic Mercury Labeled with Hg^{203}

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In the course of studying the ability of various types of organometallic compounds to undergo isotopic exchange (^{1,2}), we found that, under mild conditions, α-mercurated oxo compounds react with metallic mercury labeled with the radioactive isotope Hg^{203}.

$$R{-}Hg{-}X + {}^{*}Hg \rightleftharpoons R{-}{}^{*}Hg{-}X + Hg.$$

We have studied the interaction of metallic mercury with α-bromomercuricyclohexanone, the ethyl ester of α-bromomercuriphenylacetic acid, the l-menthyl ester of α-bromomercuriphenylacetic acid, 3-bromomercuri-3-benzylcamphor, 3-bromomercuricamphor, 1-chloromercuricamphenilone, as well as with 2-bromomercuricamphane and n-butylmercuric bromide.

The interaction of organomercury salts with metallic mercury was carried out under identical conditions. All reactions were conducted in one and the same flask, equipped with a reflux condenser, a pipette for withdrawing samples, and a Witt stirrer at 2500 ± 200 rpm. The concentrations of the organomercury compounds in all cases were 0.015 mol/l; mercury was taken in a large gram-equivalent excess (66-fold or 132-fold). The reactions were carried out in a thermostated system. Absolute benzene was used as the solvent. Only in the case of 3-bromomercuricamphor was it necessary to use dioxane, since the substance is practically insoluble in benzene.

At definite time intervals, samples were taken from the reaction mixture to determine the radioactivity of the organomercury compounds. Together with the sample, colloidal metallic mercury was always entrained; the sample was freed from it by passage through a chromatographic column with aluminum oxide. After this, the solution of the organomercury compound was evaporated to dryness under a stream of dry air, and the substance was crystallized from a suitable solvent until the literature melting point and constant radioactivity were attained. Measurements of the radioactivity of the organomercury compounds were carried out on a B-2 apparatus using MST-17 end-window counters and MS-4 γ-counters in the same manner as described by us earlier (^{2}).

Special experiments showed that, despite the heterogeneous character of the reaction, the reproducibility of the results was quite satisfactory. The discrepancies between the results of identical experiments carried out at different times do not exceed 10%.

Table 1 summarizes the results of our experiments on the isotopic exchange of various organomercury salts with metallic mercury labeled with Hg^{203}. It is evident from the table that the reactivity of α-mercurated oxo-

of the compounds with respect to metallic mercury decreases in the following order:

[structural formula of an α-bromomercury cyclohexanone derivative] $> C_6H_5$–

$>$ [structural formula of a bromomercury camphor derivative with $CH_2C_6H_5$] $>$ [structural formula of a brom

Leaving for ourselves the right to return to a detailed analysis of these results, we note that the reactivity of the indicated organomercury salts with respect to metallic mercury is determined not only by the electronic character of the radicals at the carbon atom bonded to mercury, but also, undoubtedly in a number of cases, by spatial factors. It is precisely for this reason, probably, that the 1-menthyl ester of α-bromomercuriphenylacetic acid reacts more slowly than the corresponding ethyl ester. On the other hand, when comparing the reactivity of the esters of α-bromomercuriphenylacetic acid and the *n*-propyl ester of α-chloromercuriacetic acid (which does not react with Hg^{203} at 23°),

$$C_6H_5{-}CH(HgBr){-}COOC_2H_5 > C_6H_5{-}CH(HgBr){-}COOC_{10}H_{19} > ClHg{-}CH_2{-}C(=O){-}OC_3H_7,$$

it is evident that the activating influence of the phenyl radical predominates over the steric hindrance created by it.

1-Chloromercuricamphenilone, like 2-bromomercuricamphane and *n*-butylmercuric bromide, which are not α-mercurated derivatives of oxo compounds, does not react with metallic mercury even upon heating to 100° for 40 hours. The great inertness of the mercury atom in 1-chloromercuricamphenilone, observed also in many other substitution reactions, has as yet found no satisfactory explanation. The isotope-exchange reaction found by us is apparently homolytic.

Since in the study of certain symmetrization reactions of organomercury salts (3, 4) it was established that the symmetrizing agent (NH_3, KJ) does not attack the molecules R–HgX, but binds the molecules HgX_2 formed as the result of the reversible reaction

$$2R{-}HgX \rightleftarrows R{-}Hg{-}R + HgX_2,$$

it is natural to determine whether an equilibrium of this kind plays a decisive role in our case.

Indeed, one may propose the following mechanism for the isotope-exchange reaction under consideration:

$$2\mathrm{R{-}HgX} \rightleftarrows \mathrm{R{-}Hg{-}R} + \mathrm{HgX_2} \tag{a}$$

$$\mathrm{HgX_2} + {}^{*}\mathrm{Hg} \rightleftarrows {}^{*}\mathrm{HgX_2} + \mathrm{Hg} \tag{b}$$

$$\mathrm{R{-}Hg{-}R} + {}^{*}\mathrm{HgX_2} \rightleftarrows \mathrm{R{-}{}^{*}HgX} + \mathrm{R{-}HgX} \tag{c}$$

However, two experimental facts contradict such a scheme. The first of them is that certain organomercury salts react with metallic mercury under milder conditions than with mercuric halide. Thus, for example, the ethyl ester of α-bromomercuriphenylacetic acid

Table 1

Results of isotope exchange of organomercury salts with metallic mercury

Formula of the organomercury compound	Experiment no.	0.5 h	1.0 h	2.0 h	3.0 h	4.0 h	5.0 h	6.0 h	6.5 h	10.0 h	15.0 h	20.0 h	40.0 h
[[structural formula: cyclic ketone organomercury bromide, with HgBr substituent]]	1	–	81	98	99	–	–	–	–	–	–	–	–
$C_6H_5{-}CH(HgBr){-}COOC_2H_5$	2	16	51	86	91	98	100	–	–	–	–	–	–

Formula of the organomercury compound	Experiment no.	0.5 h	1.0 h	2.0 h	3.0 h	4.0 h	5.0 h	6.0 h	6.5 h	10.0 h	15.0 h	20.0 h	40.0 h
$C_6H_5-CH(HgBr)-COOC_{10}H_{19}$	3	2	8	45	66	76	—	—	84	93	—	—	—
[[structural formula: bicyclic ketone with $CH_2C_6H_5$ and HgBr substituents]]	4	—	—	—	—	—	—	—	—	—	39	—	—
[[structural formula: bicyclic ketone organomercury bromide]]	5	—	—	—	—	—	—	—	—	—	—	17	—

Formula of the organomercury compound	Experiment no.	0.5 h	1.0 h	2.0 h	3.0 h	4.0 h	5.0 h	6.0 h	6.5 h	10.0 h	15.0 h	20.0 h	40.0 h
[[structural formula: bicyclic ketone organomercury chloride, HgCl substituent]]	6	—	—	—	—	—	—	—	—	—	—	0	0
[[structural formula: bicyclic organomercury bromide, HgBr substituent]]	7	—	—	—	—	—	—	—	—	—	—	0	0
$CH_3CH_2CH_2CH_2$—HgBr	8	—	—	—	—	—	—	—	—	—	—	—	0

Notes. 1. In all experiments the concentration of the organomercury compound was 0.015 mole/l. In experiments nos. 1–3, mercury was taken in 66-fold excess; in experiments 4–8, in 132-fold excess. Dioxane was used as the solvent in experiment no. 5; in all the other experiments, benzene. Experiments nos. 1–6 were carried out at 23°, experiments nos. 7 and 8 at 80°.

2. In all cases the table gives the percentage of exchange relative to the equilibrium value.

[[beginning of sentence continued from preceding page]] reacts readily in benzene in the cold with Hg, but does not react under these conditions with $^*HgBr_2$.

The second fact is that, in all the cases we studied, the formation of even traces of monohalide mercury was not detected. Meanwhile, if the reaction proceeded through equilibrium (a), then some amount of monohalide mercury (along with the symmetrical organomercury compound) would inevitably be obtained as a result of the reaction:

$$Hg + HgX_2 \rightarrow Hg_2X_2.$$

Thus, the isotope-exchange reaction under consideration proceeds not through the stage of equilibrium (a), but metallic mercury reacts directly with the organomercury salt R—HgX.

Although the reaction is probably homolytic, it is unlikely to proceed through the stage of formation of free radicals. Isotopic exchange

proceeds in the cold under such mild conditions that decomposition of organomercury compounds with the formation of free radicals has never been observed.

The fact that isotope exchange proceeds with retention of the stereochemical configuration at the carbon atom bonded to the mercury atom also argues against the formation of free radicals as kinetically independent particles. This fact was established by us using the example of diastereomeric *l*-menthyl esters of α-bromomercuriphenylacetic acid, and also using the example of cis- and trans-2-methoxycyclohexylmercury chlorides.

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