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Abstract

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ISOTOPE-EXCHANGE REACTION OF SUBSTITUTED BENZYLMERCURY BROMIDES WITH MERCURIC BROMIDE LABELED WITH THE RADIOACTIVE ISOTOPE Hg^{203}

In connection with an investigation of the mechanism of electrophilic substitution at a saturated carbon atom, we have recently studied, in a number of examples ([1-6]), the isotope-exchange reaction of organomercury salts with mercuric halides

$$R_1R_2R_3{-}HgX + X{-}Hg^{203}X \rightleftharpoons R_1'R_2R_3{-}Hg^{203}X + HgX_2.$$

It has been possible to study most thoroughly the kinetics of the readily occurring isotope-exchange reaction of esters of α-bromomercuriarylacetic acids ($R_1 = Ar,\ R_2 = COOAlk,\ R_3 = H$) with radioactive mercuric bromide ([3,6]).

In the present work we describe the results of studying the kinetics of the isotope-exchange reaction in simpler, benzyl, organomercury compounds ($R_1 = Ar,\ R_2 = R_3 = H$) with mercuric bromide labeled with the radioactive isotope Hg^{203}

$$X{-}C_6H_4{-}CH_2{-}HgBr + Hg^{203}Br_2 \rightleftharpoons X{-}C_6H_4{-}CH_2{-}Hg^{203}Br + HgBr_2.$$

First of all, it was found that replacement of the carbalkoxy group by hydrogen, i.e., the transition from esters of α-bromomercuriarylacetic acids to benzylmercury bromides, leads to a considerable decrease in the rate of the isotope-exchange reaction under consideration.

In all the solvents we tested (toluene, bromobenzene, alcohol, acetone, dioxane, acetonitrile, N,N-dimethylformamide, glacial acetic and formic acids, isoamyl

acetate, isoamyl ether, carbon tetrachloride, pyridine), either the reaction proceeds too slowly, or decomposition of the organomercury salt occurs. The exception is quinoline, in which isotope exchange proceeds at 70° at a rate convenient for kinetic measurements and without decomposition of the organomercury salt. Under these conditions, naturally, the mercuric bromide is present, at least in part, in the form of a complex with quinoline.

The isotope-exchange reaction of benzylmercury bromide with mercuric bromide has overall second order and first order with respect to each of the components. Thus it is a bimolecular reaction of electrophilic substitution at a saturated carbon atom (S_E2). $K_2 = 0.148$ L mol^{-1} hr^{-1}.

Apparently, it is not free mercuric bromide that reacts with benzylmercury bromide, but its complex with quinoline (B :)*; the molecules of this complex must be more polar than the molecules of mercuric bromide:

$$\begin{array}{c} \overset{\delta^+}{\mathrm{B}:\cdots\mathrm{Hg}}\overset{\delta^-}{-\mathrm{Br}} \\ | \\ \mathrm{Br} \end{array}$$

* The possibility is not excluded that the organomercury salt may also participate in the reaction in the form of the complex $\mathrm{R{-}HgX \cdot C_9H_7N}$.

The catalytic effect of bases on the rate of isotope-exchange reactions of the type

$$\mathrm{RHgX + Hg^{203}X_2 \rightleftharpoons RHg^{203}X + HgX_2},$$

which we have repeatedly noted earlier ([1,2]), is apparently due in part to the fact that the complex of the base with mercuric halide ($\mathrm{B : HgX_2}$) is a stronger electrophilic reagent than the low-polarity molecule of mercuric halide.

A second possible reason for the catalytic action of bases consists in solvation by the base of the mercury atom leaving the molecule of the organomercury compound.

Taking these assumptions into account, the mechanism of the isotope-exchange reaction of benzylmercury bromide with mercuric bromide in quinoline may be expressed by the following scheme*:

$$R_2-\mathrm{C}\begin{matrix}R_1\\-\\R_3\end{matrix}-\mathrm{HgBr} + \mathrm{B : Hg^{203}Br_2} \rightleftharpoons \left[\begin{matrix}\text{cyclic activated complex (AI)}\\ \text{with HgBr, } \mathrm{Hg^{203}Br}, \text{ B :}\end{matrix}\right] \rightleftharpoons \left[\begin{matrix}\text{cyclic activated complex (AII)}\\ \text{with B : HgBr and } \mathrm{Hg^{203}Br}\end{matrix}\right] \rightleftharpoons$$

$$R_2-\mathrm{C}\begin{matrix}R_1\\-\\R_3\end{matrix}-\mathrm{Hg^{203}Br} + \mathrm{B : HgBr_2} \qquad (R_1 = \mathrm{C_6H_5},\ R_2 = R_3 = \mathrm{H}.\ \mathrm{B} = \text{quinoline})$$

It remains an open question whether the base molecule B : passes within the activated complex from the radioactive mercury atom to the nonradioactive one, or whether the process (AI) → (AII) is a process in which the nonradioactive mercury atom departs with simultaneous solvation by another base molecule. Of course, this question is removed if it is not the molecule of the organomercury salt that participates in formation of the transition state, but rather its complex with quinoline, $R_1R_2R_3C$—HgBr : B.

The activation energy of the reaction under consideration was found to be 18.8± 0.9 kcal/mole. The rate constant K_2 is 0.066; 0.148; 0.323; 0.641 $l \cdot mol^{-1} \cdot h^{-1}$ at temperatures of 60; 70; 80, and 88°, respectively.

We studied the influence of structural factors on the rate of the reaction under consideration using a series of para-substituted benzylmercury bromides:

$$X{-}C_6H_4{-}CH_2{-}HgBr + Hg^{203}Br_2 \rightleftharpoons X{-}C_6H_4{-}CH_2{-}Hg^{203}Br + HgBr_2$$

$$(X = F,\ Cl,\ H,\ CH_3,\ (CH_3)_2CH)$$

All reactions were carried out in quinoline** at equimolecular concentrations of the reagents, equal to $5.4 \cdot 10^{-2}$ mol/l, and at a temperature of 70°.

* The cyclic transition state shown in this scheme for reactions of the type under consideration is the more probable the less polar the solvent. Since quinoline is not a nonpolar solvent, the possibility of a noncyclic transition state of type (AIII) cannot be considered excluded:

$$R_2 - \underset{R_3}{\overset{R_1}{C}} - HgBr + B : Hg^{203}Br_2 \rightleftharpoons \left[\begin{array}{c}\text{noncyclic transition state}\\ \text{(AIII)}\end{array}\right] \rightleftharpoons R_2 - \underset{R_3}{\overset{R_1}{C}} - Hg^{203}Br + HgBr^+ + Br^- + B :$$

$$\rightleftharpoons B : HgBr_2$$

** Quinoline was kept for a long time over solid caustic potash and, before each experiment, was distilled over zinc dust. The fraction with b.p. 118-119° at 20 mm Hg was collected.

Solutions of the organomercury compound and mercuric bromide, brought to the experimental temperature in a thermostated system, were mixed together, and at definite time intervals samples of the solution were taken from the reaction mixture.

Table 1

X—C_6H_4—CH_2—HgBr

X	Reaction time t, h	Layer activity, imp/min (aqueous)	Layer activity, imp/min (organic)	Degree of isotope exchange F	$-\lg(1-F)$	K_2, l/mol · h
$X = (CH_3)_2CH$	10	2000	258	0.23	0.1135	0.237
$X = (CH_3)_2CH$	15	1824	355	0.33	0.1739	0.237
$X = (CH_3)_2CH$	20	1828	472	0.41	0.2291	0.237
$X = (CH_3)_2CH$	25	1709	538	0.48	0.2840	0.237
$X = (CH_3)_2CH$	30	1611	635	0.56	0.3565	0.237
$X = (CH_3)_2CH$	35	1474	642	0.61	0.4089	0.237
$X = (CH_3)_2CH$	40	1440	707	0.68	0.4949	0.237
$X = (CH_3)_2CH$	45	1408	755	0.70	0.5229	0.237
$X = (CH_3)_2CH$	50	1459	880	0.75	0.6021	0.237
$X = (CH_3)_2CH$	60	1256	837	0.80	0.6990	0.237
$X = CH_3$	6	2217	183	0.15	0.0706	0.206
$X = CH_3$	17	3317	653	0.33	0.1739	0.206
$X = CH_3$	20	2741	594	0.36	0.1938	0.206
$X = CH_3$	25	2489	678	0.43	0.2441	0.206
$X = CH_3$	30	2711	905	0.50	0.3010	0.206
$X = CH_3$	35	2103	814	0.56	0.3565	0.206
$X = CH_3$	40	2761	1185	0.60	0.3979	0.206
$X = CH_3$	45	2082	919	0.61	0.4089	0.206
$X = CH_3$	50	2208	1154	0.69	0.5086	0.206
$X = CH_3$	55	2280	1182	0.68	0.4949	0.206

X	Reaction time t, h	Layer activity, imp/min (aqueous)	Layer activity, imp/min (organic)	Degree of isotope exchange F	$-\lg(1-F)$	K_2, l/mol · h
$X = H$	10	2420	170	0.13	0.0605	0.148
$X = H$	20	2485	388	0.27	0.1376	0.148
$X = H$	30	1963	447	0.37	0.2007	0.148
$X = H$	42	2153	708	0.50	0.3010	0.148
$X = H$	50	1726	648	0.55	0.3468	0.148
$X = H$	60	1743	798	0.63	0.4318	0.148
$X = H$	74	1496	827	0.71	0.5376	0.148
$X = H$	94	1331	856	0.78	0.6576	0.148
$X = Cl$	10	2210	174	0.15	0.0706	0.131
$X = Cl$	20	2020	277	0.24	0.1192	0.131
$X = Cl$	30	1926	390	0.34	0.1938	0.131
$X = Cl$	40	1701	473	0.44	0.2518	0.131
$X = Cl$	50	1616	558	0.51	0.3098	0.131
$X = Cl$	60	1453	587	0.58	0.3768	0.131
$X = Cl$	79	1304	678	0.68	0.4949	0.131
$X = F$	6	2349	86	0.07	0.0315	0.121
$X = F$	20	3146	418	0.23	0.1135	0.121
$X = F$	25	3007	505	0.29	0.1487	0.121
$X = F$	30	2818	544	0.32	0.1675	0.121
$X = F$	35	2719	648	0.38	0.2076	0.121
$X = F$	40	2241	573	0.41	0.2291	0.121
$X = F$	45	2572	732	0.44	0.2518	0.121
$X = F$	50	2631	811	0.47	0.2757	0.121
$X = F$	55	2673	962	0.53	0.3279	0.121

Then the sample of the quinoline solution was diluted 10-fold with toluene, and this solution was treated with a saturated solution of sodium bromide in water to remove mercuric bromide. The aqueous layer containing mercuric bromide was separated from the organic layer containing the organomercury salt, and the activity of each layer was determined on the B-2 apparatus.

The results of the isotope exchange are given in Table 1 and in Fig. 1.

From these results* it is seen that the substituents X are arranged in the following order according to their accelerating influence on the isotope-exchange reaction under consideration (the half-exchange periods, in hours, are given in parentheses)**:

$$\underset{(53)}{\mathrm{F}} < \underset{(49)}{\mathrm{Cl}} < \underset{(43)}{\mathrm{H}} < \underset{(31)}{\mathrm{CH_3}} < \underset{(27)}{(\mathrm{CH_3})_2\mathrm{CH}}$$

$\mathrm{H_3C^-{-}C_6H_4{-}\overset{\delta-}{C}H_2{-}HgBr}$, $\mathrm{H{-}C_6H_4{-}CH_2{-}HgBr}$, $\mathrm{F{-}C_6H_4{-}\overset{\delta+}{C}H_2{-}HgBr}$

The observed dependence of the rate of the S_E2-reaction under consideration on the nature of substituent X is quite understandable: the influence of electron-donating substituents is expressed in the appearance, on the carbon atom bonded to mercury, of a partial negative charge, whereas the influence of electron-withdrawing substituents is expressed in the appearance of a partial positive charge (apparently, mainly at the moment of reaction), as compared with unsubstituted benzylmercuric bromide. In the first case, attack of the organomercury compound by the electrophilic complex $\mathrm{B:HgBr_2}$ is facilitated; in the second, it is hindered.

Fig. 1. Isotope exchange of $\mathrm{XC_6H_4CH_2HgBr}$ with $\mathrm{Hg^{203}Br_2}$ in quinoline at 70°.
1–*n*-$\mathrm{FC_6H_4CH_2HgBr}$, 2–*n*-$\mathrm{CH_3C_6H_4CH_2HgBr}$, 3–*n*-iso-$\mathrm{C_3H_7C_6H_4CH_2HgBr}$, 4–$\mathrm{C_6H_5CH_2HgBr}$, 5–*n*-$\mathrm{ClC_6H_4CH_2HgBr}$

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1. O. A. Reutov, *Izv. AN SSSR, OKhN*, **1958**, 684.

2. O. A. Reutov, T. A. Smolina, Yu. Yan-Tsei, Yu. N. Bubnov, *Nauchn. dokl. vyssh. shkoly, Khimiya i khim. tekhnol.*, No. 2, 324 (1958).

3. O. A. Reutov, Yu. Yan-Tsei, I. P. Beletskaya, in: *Kinetics and Catalysis*, 1960, p. 43.

4. O. A. Reutov, *Angew. Chem.*, **21**, 688 (1957).

5. O. A. Reutov, *Rec. Chem. Progr.*, No. 3 (1961).

6. O. A. Reutov, V. I. Sokolov, I. P. Beletskaya, *DAN*, **136**, 631 (1961).

* Isotope-exchange experiments carried out under identical conditions, but at different times, gave good reproducibility of the results: the straight lines $\lg(1-F) = f(t)$ for each organomercury compound practically coincided; the scatter of points for each straight line did not exceed on average $\pm 3\%$.

** We note that the dependence of the rate of this reaction on the character of substituents X is the reverse of the dependence studied by one of us together with V. I. Sokolov and I. P. Beletskaya[6] for the monomolecular reaction (S_E1) of isotope exchange of the ethyl ester of α-bromomercuriphenylacetic acid with mercuric bromide.

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