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Abstract

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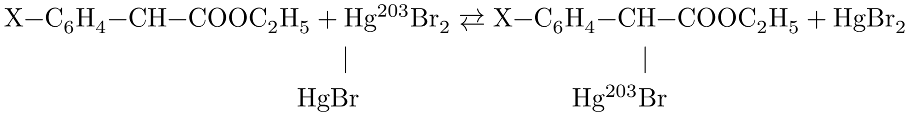
ON THE QUESTION OF THE MECHANISM OF ISOTOPIC EXCHANGE OF ORGANOMERCURY SALTS WITH MERCURIC HALIDE

In studying the isotopic exchange of esters of α-bromomercuriarylacetic acids with mercuric halide:



$$\underset{\displaystyle\text{HgBr}}{X{-}C_6H_4{-}\underset{|}{CH}{-}COOC_2H_5} + Hg^{203}Br_2 \rightleftarrows \underset{\displaystyle Hg^{203}Br}{X{-}C_6H_4{-}\underset{|}{CH}{-}COOC_2H_5} + HgBr_2$$

it had previously been established (^{1}-^{5}) that the reaction mechanism depends substantially on the medium. In such solvents as ethanol and pyridine, the reaction proceeds by the mechanism of bimolecular electrophilic substitution (S_E2). The use of 70% aqueous dioxane and dimethyl sulfoxide (DMSO) as solvents made it possible for the first time to direct the reaction along a monomolecular mechanism (S_E1):

$$\begin{array}{lcll}
R{-}HgX & \overset{\text{slow}}{\underset{\longleftarrow}{\longrightarrow}} & R:^- \;+ HgX^+ & \text{(ion pair)} \\
 & & \quad\updownarrow \; Hg^{203}X_2 & \\
 & & \qquad\updownarrow \; \text{fast} & \\
R{-}Hg^{203}X & \overset{\text{fast}\ (-)}{\underset{\longleftarrow}{\longrightarrow}} & R: \quad Hg^{203}X^+. &
\end{array}$$

We studied isotopic exchange of the type under consideration in DMSO at 70° for benzylmercury halides—compounds with a less reactive C–Hg bond, which usually react very slowly by the S_E2 mechanism in quinoline (^{6}, ^{7}):

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

Fig. 1. Dependence of the constant K_2 on the concentration of KBr at $[HgBr_2] = [C_6H_5{-}CH_2HgBr] = 0.06\ \text{mol}\cdot\text{l}^{-1}$

Figure 1

Figure 1: Figure 1

Fig. 2 and Fig. 3: kinetic plots

Figure 2: Fig. 2 and Fig. 3: kinetic plots

It turned out that isotopic exchange in DMSO proceeds considerably faster than in quinoline; however, the reaction mechanism still remains bimolecular (first order with respect to the organomercury salt and first order with respect to mercuric halide). The reaction rate constants K_2 are respectively: $K_{2(\mathrm{DMSO})} = 0.37\ \mathrm{l} \cdot \mathrm{mol}^{-1} \cdot \mathrm{h}^{-1}$, $K_{2(\mathrm{quinoline})} = 0.13\ \mathrm{l} \cdot \mathrm{mol}^{-1} \cdot \mathrm{h}^{-1}$. Additions of potassium bromide exert a substantial influence on the course of isotopic exchange of benzylmercury halides in DMSO medium.

First of all, it should be noted that isotopic exchange in the presence of potassium bromide proceeds considerably faster. Study of the kinetics of the isotopic-exchange reaction in the presence of potassium bromide showed that, for example, at concentrations of potassium bromide equal to the concentrations of mercuric bromide, the bimolecularity of the process is preserved (first order with respect to the organomercury salt and first order with respect to the mercuric halide salt), with $K_2 = 1.52\ \mathrm{mol}^{-1} \cdot \mathrm{l} \cdot \mathrm{h}^{-1}$.

Increasing the concentration of potassium bromide promotes an increase in the rate of the isotopic-exchange reaction. At concentrations of mercuric bromide and benzylmercury bromide equal to $0.06\ \mathrm{mol} \cdot \mathrm{l}^{-1}$, the reaction-rate constant increases, as the concentration of potassium bromide increases, as follows:

thus (see Fig. 1):

[KBr], $\mathrm{mol} \cdot \mathrm{l}^{-1}$	0	0.06	0.12	0.18
$10^2 \cdot K_2$, $\mathrm{l} \cdot \mathrm{mol}^{-1} \cdot \mathrm{h}^{-1}$	37	148	1444	2139

At high concentrations of potassium bromide (for example, $[\mathrm{KBr}]/[\mathrm{HgBr_2}]$ equal to 2 and higher), the second-order reaction rate constant K_2 is not maintained sufficiently satisfactorily. This may be explained either by a salt effect or by the fact that, at relatively high concentrations of potassium bromide, the reaction may proceed in parallel by two mechanisms, S_E2 and S_E1, owing to an increase in the lability of the C–Hg bond in the reacting organomercury complex. This question requires further clarification.

Fig. 2. Dependence of the rate of isotopic exchange on the nature of substituent X at $[\mathrm{HgBr_2}] = [\mathrm{X{-}C_6H_4{-}CH_2HgBr}] = 0.06\ \mathrm{mol} \cdot \mathrm{l}^{-1}$: 1 $-\mathrm{CH_3}$; 2 $-(\mathrm{CH_3})_2\mathrm{CH}$; 3 –H; 4 –F; 5 –Cl.

Fig. 3. Dependence of the rate of isotopic exchange on the nature of substituent X in the presence of KBr at $[\mathrm{HgBr_2}] = [\mathrm{X{-}C_6H_4{-}CH_2{-}HgBr}] = 0.06\ \mathrm{mol} \cdot \mathrm{l}^{-1}$;

[KBr] = 0.09 mol · l^{-1}: 1 –Cl; 2 –F; 3 –H; 4 –CH_3; 5 –$(CH_3)_2CH$.

The study of the influence of the nature of substituents X located in the para position of the benzene ring showed that this influence has an opposite character for the reaction catalyzed by additions of KBr and for the reaction proceeding in the absence of KBr.

For isotopic exchange occurring in DMSO without additions of KBr, the influence of substituents X located in the para position of the benzene nucleus on the reaction rate remained the same as had been found previously for this same isotopic-exchange reaction in quinoline, although the exchange rate in DMSO was considerably higher than in quinoline ([6]).

We give the half-exchange periods for various para-substituted benzylmercury bromides $X—C_6H_4—CH_2—HgBr$ at 70° and concentrations $[HgBr_2] = [X—C_6H_4—CH_2—HgBr] = 0.06$ mol/l:

X	Cl	F	H	CH_3	$CH(CH_3)_2$
$T_{1/2}$, h	19	19	17	13	13

In terms of their accelerating influence, the substituents are arranged in the following order:

$$Cl,\ F < H < CH_3,\ CH(CH_3)_2$$

(see Fig. 2). When isotopic exchange is carried out in the presence of potassium bromide, the pattern of substituent influence changes sharply. Along with a large acceleration of the reaction, the influence of the substituent changes to the opposite (see Table 1).

In this case, the substituents are arranged in the following order according to their accelerating influence:

$$(CH_3)_2CH < CH_3,\ H < F,\ Cl$$

(see Fig. 3).

An increase in the concentration of potassium bromide leads to an acceleration of the reaction and to an increase in the degree of difference in the influence of the substituents. Thus, for example, at potassium bromide concentrations of 0.09 and 0.12 mole · l^{-1}, the ratios

Table 1

[KBr], mole · l^{-1}	$[HgBr_2]$, mole · l^{-1}	$[X–C_6H_4–CH_2–HgBr]$, mole · l^{-1}	X	Cl	F	H	CH_3	$CH(CH_3)_2$
0.09	0.06	0.06	$T_{1/2}$, min	24	35	45	45	50

[KBr], mole · l^{-1}	[$HgBr_2$], mole · l^{-1}	[$X{-}C_6H_4{-}CH_2{-}HgBr$], mole · l^{-1}	X	Cl	F	H	CH_3	$CH(CH_3)_2$
0.12	0.06	0.06	$T_{1/2}$, min	10	18	25	25	30

of the half-exchange periods for para-isopropyl and para-chlorobenzylmercury bromides are respectively equal to 2 and 3. The influence of KBr additions can be explained by the fact that complexes of mercuric bromide and of the organomercury compound with the bromide anion ($HgBr_3^-$ and $RHgBr_2^-$) are formed in the system, facilitating isotopic exchange; moreover, it is evident that the second complex should be more difficult to form (i.e., at higher KBr concentrations).

Thus, apparently, it is necessary to take into account the possibility of two parallel reactions proceeding (of the type proposed by Ingold and co-workers ([8]) for one- and two-anion catalysis of monoalkyl isotopic exchange of alkylmercury halides).

$$X{-}C_6H_4{-}CH_2HgBr + {}^{203}HgBr_3^- \rightleftharpoons \left[X{-}C_6H_4{-}CH_2\ldots\substack{\cdots HgBr\\ {}^{203}HgBr_2}\cdots Br\right]^- \rightleftharpoons X{-}C_6H_4{-}CH_2{}^{203}HgBr + HgBr_3^-$$

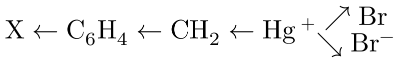
(IIA)

$$X{-}C_6H_4{-}CH_2HgBr_2^- + {}^{203}HgBr_3^- \rightleftharpoons \left[X{-}C_6H_4{-}CH_2\ldots\substack{\cdots HgBr_2\\ {}^{203}HgBr_2}\cdots Br\right]^= \rightleftharpoons X{-}C_6H_4{-}CH_2{}^{203}HgBr_2^- + HgBr$$

(IIB)

If two-anion catalysis is stronger than one-anion catalysis, then the reaction rate should depend substantially on the concentration of the $RHgBr_2^-$ complex, i.e., the higher the concentration of the organomercury complex, the higher the rate of the isotopic-exchange reaction. It is evident that substituents in the benzene ring should affect the ease of formation and, consequently, the concentration of this complex.

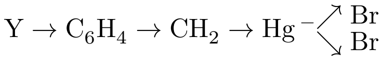
From this point of view it becomes understandable why, in isotopic exchange catalyzed by KBr, we observe the reverse order of substituent influence in comparison with the uncatalyzed reaction. Naturally, electron-withdrawing substituents, by drawing electron density away from the mercury atom, should facilitate formation of the complex with the bromide anion. (Compared with unsubstituted benzylmercury bromide) (see A):

(A) 

$$X \leftarrow C_6H_4 \leftarrow CH_2 \leftarrow Hg^{+}\begin{matrix}\nearrow Br \\ \searrow Br^{-}\end{matrix}$$

approach facilitated

(B) $H{-}C_6H_4{-}CH_2{-}Hg{-}Br$

(V) 

$$Y \rightarrow C_6H_4 \rightarrow CH_2 \rightarrow Hg^{-}\begin{matrix}\nearrow Br \\ \searrow Br\end{matrix}$$

approach hindered

Conversely, in the case of electron-donor substituents, formation of a covalent bond between the bromide anion and the mercury atom should be hindered (B)*.

Experimental Part

Organomercury salts were obtained through organomagnesium compounds. Mercuric bromide labeled with the radioactive isotope Hg^{203} was obtained from radioactive metallic mercury and bromine, followed by crystallization from distilled water.

Potassium bromide (analytical grade) was recrystallized from distilled water and dried at 110° for several hours.

Dimethyl sulfoxide, purified by the procedure of ([5]), had the following constants: b.p. 70° (at 9 mm Hg), m.p. 17—18°, $n_D^{19.5} = 1.4793$. Literature data: b.p. 70° (at 9 mm Hg), m.p. 18.5° ([5]); $n_D^{19.5} = 1.4793$ ([5]).

The procedure for the kinetic measurements was analogous to that described by us earlier ([7]).

Special experiments established that, during the separation of the organomercury compound and mercuric bromide, no exchange occurs.

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* As a possible anion participating in two-anion catalysis, together with $RHgBr_2^-$, Ingold and co-workers ([8]) consider the anion $HgBr_4^{2-}$.

Our results on the effect of substituents X in the benzene ring on the reaction rate speak in favor of the anion $RHgBr_2^-$. The general picture of the mechanism should not change even if the latter bromide anion is bound somewhat more strongly in transition state II B than in the initial anion $X—C_6H_4—CH_2—HgBr_2^-$.

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

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