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Abstract

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ON THE MONOMOLECULAR MECHANISM OF ISOTOPIC EXCHANGE OF BENZYLMERCURY HALIDES WITH RADIOACTIVE MERCURIC HALIDE

In the last decade interest has sharply increased in the study of electrophilic substitution reactions. It is obvious that the regularities obtained in this way may directly or indirectly contribute to the elucidation of a number of general questions concerning mechanisms of substitution reactions at a saturated carbon atom. A number of authors have described reactions of bimolecular electrophilic substitution (S_E2) at a saturated carbon atom. At the same time, until quite recently S_E1-reactions were unknown.

In studying the influence of the nature of the solvent on the isotopic-exchange reaction:

$$\mathrm{RR'R''C-HgX+Hg^{203}X_2 \rightleftharpoons RR'R''C-Hg^{203}X+HgX_2}$$

one of us, together with co-workers (^{1,2}), succeeded for the first time in carrying out an S_E1-reaction (first kinetic order with respect to the organomercury compound and zero order with respect to mercuric halide) for the case of the ethyl ester of α-bromomercuriphenylacetic acid, using solvents with high ionizing power. Dimethyl sulfoxide (DMSO) proved especially suitable for this purpose.*

However, in studying the isotopic exchange in DMSO of benzylic organomercury compounds (less reactive in S_E-reactions than esters of α-bromomercuriphenylacetic acid), we found (^{3}) that the reaction proceeds not by a monomolecular but by a bimolecular mechanism

$$\mathrm{X{-}C_6H_4{-}CH_2{-}HgBr + Hg^{203}Br_2 \xrightleftharpoons{DMSO} X{-}C_6H_4{-}CH_2{-}Hg^{203}Br + HgBr_2 \quad S_E2}$$

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

i.e., just as when quinoline is used as the solvent (4). Obviously, despite the high ionizing power of DMSO, in the present case it is insufficient to ionize the strong C—Hg bond with formation of an ion pair:

$$> \mathrm{C} : \mathrm{HgBr} \rightleftharpoons > \mathrm{C}^{(-)} : \mathrm{Hg}^{(+)}\mathrm{Br}$$

It is natural to assume that the probability of an S_E1-mechanism for the reaction under consideration in DMSO should increase in the case where the carbanion formed as a result of ionization possesses greater stability owing to delocalization of the negative charge, for example.

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* In DMSO it proved possible to carry out an S_E1-mechanism also for protolysis reactions (under the action of HX or DX) of organomercury compounds with a mercury atom attached to an olefinic or aromatic carbon atom:

$$\mathrm{RHC{=}CH{-}HgX} + \mathrm{DX} \rightarrow \mathrm{RHC{=}CHD} + \mathrm{HgX_2}$$

$$\mathrm{Ar{-}HgX} + \mathrm{HX} \rightarrow \mathrm{Ar{-}H} + \mathrm{HgX_2}.$$

All these reactions are first order with respect to the organomercury compound and zero order with respect to hydrogen halide.

structural factors:

$$\mathrm{X{-}C_6H_4{-}}\overset{(+)}{\mathrm{CH_2}} \quad \mathrm{HgBr}^{(-)}$$

The most suitable object for carrying out an S_E1-mechanism should be substituted benzylmercury halides with strong electron-withdrawing substituents in the benzene ring.

Experimental verification confirmed this supposition.
We studied the kinetics of isotopic exchange of *p*-nitrobenzylmercury bromide with radioactive mercuric bromide in DMSO. As we had assumed, the reaction has an overall first order (first order with respect to the organomercury compound and zero order with respect to mercuric bromide).

Thus, we succeeded in carrying out an S_E1-reaction of the type under consideration for benzyl systems, purposefully using structural factors and the ionizing ability of the solvent.

The reaction mechanism may be expressed by the following scheme:

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

$$\begin{tikzcd}
O_2N{-}C_6H_4{-}CH_2{-}HgBr \arrow[r, shift left, "\text{slow}"] & O_2N{-}C_6H_4{-}\overset{(+)}{C}H_2\ Br^{(-)}Hg \arrow[l, shift left, "\text{fast}"] \arrow[d, shift right, "HgBr_2\ \text{fast}"'] \\
O_2N{-}C_6H_4{-}CH_2{-}Hg^{203}Br \arrow[r, shift left, "\text{fast}"] & O_2N{-}C_6H_4{-}\overset{(+)}{C}H_2\ Br^{(-)}Hg^{203} \arrow[l, shift left, "\text{slow}"] \arrow[u, shift right, "Hg^{203}Br_2\ \text{fast}"']
\end{tikzcd}$$

Experimental Part

The kinetics of the reaction was studied in the reagent concentration range 0.015 –0.18 mole/l at temperatures of 40, 50, 60, and 70°. Kinetic measurements were carried out by the previously developed method of paper radiochromatography (^{5}).

Fig. 1. Isotopic exchange of *p*-$NO_2C_6H_4CH_2HgBr$ with $Hg^{203}Br_2$ in DMSO at 70° and at different equimolecular concentrations.
1—0.03; 2—0.06; 3—0.09; 4—0.12 mole/liter.

Fig. 2. Dependence of the exchange rate constant on the concentration of one of the components.
1—$\lg R = f(C_{NO_2C_6H_4CH_2HgBr})$; 2—$\lg R = f(C_{HgBr_2})$

Weighed portions of mercuric bromide and *p*-nitrobenzylmercury bromide* were dissolved in 1-2 ml of DMSO, and the resulting solutions were placed in a thermostatted system. At definite time intervals, samples of the ra—

* *p*-Nitrobenzylmercury bromide was obtained by shaking an acetone solution of *p*-nitrobenzyl bromide with metallic mercury under ultraviolet irradiation. M.p. 181-182° (from dioxane). Analytical results:

Found, %: C 20.50; H 1.50; Hg 47.84; Br 19.09
$C_7H_6BrHgNO_2$. Calculated, %: C 20.18; H 1.45; Hg 48.14; Br 19.18

The preparation of mercuric bromide labeled with the radioactive isotope Hg^{203} and the purification of DMSO were described by us earlier (^{3}).

Table 1

C_{HgBr_2}, mol/l	$C_{NO_2C_6H_4CH_2HgBr}$, mol/l	Exchange time, h	A_{HgBr_2}, imp/min	$A_{NO_2C_6H_4CH_2HgBr}$, imp/min	Degree of exchange F, %	Initial rate $R \cdot 10^3$, mol $\cdot$ l^{-1} $\cdot$ h^{-1}	K_{HgBr}, h^{-1}	K_2, l $\cdot$ mol^{-1} $\cdot$ h^{-1}	C_{HgBr_2}, mol/l	$C_{NO_2C_6H_4CH_2HgBr}$, mol/l	Exchange time, h	A_{HgBr_2}, imp/min	$A_{NO_2C_6H_4CH_2HgBr}$, imp/min	Degree of exchange F, %	Initial rate $R \cdot 10^3$, mol $\cdot$ l^{-1} $\cdot$ h^{-1}	K_{HgBr}, h^{-1}	K_2, l $\cdot$ mol^{-1} $\cdot$ h^{-1}
0.03	0.03	0.5	3349	147	8	0.41	0.136	4.5	0.06	0.12	0.5	5518	1077	24	0.71	0.143	2.3
0.03	0.03	1	3098	310	18	0.41	0.136	4.5	0.06	0.12	1	4264	1520	39	0.71	0.143	2.3
0.03	0.03	2	2832	740	41	0.41	0.136	4.5	0.06	0.12	1.5	2650	1325	50	0.71	0.143	2.3
0.03	0.03	3.5	2474	1072	61	0.41	0.136	4.5	0.06	0.12	2.5	1873	1321	62	0.71	0.143	2.3
0.03	0.03	5.5	2306	1465	78	0.41	0.136	4.5	0.06	0.12	3.5	1920	2012	77	0.71	0.143	2.3
0.03	0.03	8	1886	1466	88	0.41	0.136	4.5									
0.06	0.06	0.0	4312	73	3	0.82	0.136	2.3	0.03	0.06	0.5	1382	123	12	0.75	0.124	4.1
0.06	0.06	0.5	4904	321	12	0.82	0.136	2.3	0.03	0.06	1	1333	268	25	0.75	0.124	4.1
0.06	0.06	1.5	3369	659	33	0.82	0.136	2.3	0.03	0.06	1.5	2209	738	38	0.75	0.124	4.1
0.06	0.06	3	3000	1308	61	0.82	0.136	2.3	0.03	0.06	2	1895	1119	52	0.75	0.124	4.1
0.06	0.06	4	2375	1205	67	0.82	0.136	2.3	0.03	0.06	2.5	1727	1181	61	0.75	0.124	4.1
0.06	0.06	6	2236	1534	81	0.82	0.136	2.3	0.03	0.06	3	1613	1516	73	0.75	0.124	4.1
0.06	0.06	7.7	2285	1793	88	0.82	0.136	2.3	0.03	0.06	4	1466	1595	78	0.75	0.124	4.1
									0.03	0.06	4.5	1408	1692	82	0.75	0.124	4.1
									0.03	0.06	5	1230	1528	83	0.75	0.124	4.1
0.09	0.09	0.5	4527	284	12	1.22	0.136	1.5	0.12	0.06	0.5	6925	195	8	0.79	0.132	1.1
0.09	0.09	1.5	3367	685	34	1.22	0.136	1.5	0.12	0.06	1	6516	343	15	0.79	0.132	1.1
0.09	0.09	2	3247	889	43	1.22	0.136	1.5	0.12	0.06	1.5	6301	572	25	0.79	0.132	1.1
0.09	0.09	3	3180	1237	56	1.22	0.136	1.5	0.12	0.06	2	6144	735	32	0.79	0.132	1.1
0.09	0.09	4.5	2911	1569	70	1.22	0.136	1.5	0.12	0.06	2.5	6067	920	39	0.79	0.132	1.1
0.09	0.09	6	2650	1696	78	1.22	0.136	1.5	0.12	0.06	3	5878	1098	47	0.79	0.132	1.1
0.09	0.09	7	2707	2074	87	1.22	0.136	1.5	0.12	0.06	3.5	4464	987	54	0.79	0.132	1.1
									0.12	0.06	4.5	5117	1233	58	0.79	0.132	1.1
									0.12	0.06	5	4595	1170	61	0.79	0.132	1.1
									0.12	0.06	5	4859	1296	63	0.79	0.132	1.1
0.12	0.12	0.0	2692	30	2	1.63	0.136	1.1	0.18	0.06	0.5	10000	242	9	0.81	0.135	0.7
0.12	0.12	0.5	1564	94	11	1.63	0.136	1.1	0.18	0.06	1	9496	364	15	0.81	0.135	0.7
0.12	0.12	1	2875	409	25	1.63	0.136	1.1	0.18	0.06	1.5	8800	565	24	0.81	0.135	0.7
0.12	0.12	1.5	3142	659	35	1.63	0.136	1.1	0.18	0.06	2	8156	672	30	0.81	0.135	0.7
0.12	0.12	2	2267	587	41	1.63	0.136	1.1	0.18	0.06	2.5	7970	735	34	0.81	0.135	0.7
0.12	0.12	2.5	2862	987	51	1.63	0.136	1.1	0.18	0.06	3.5	7763	976	45	0.81	0.135	0.7
0.12	0.12	3	1906	826	58	1.63	0.136	1.1	0.18	0.06	4	7907	1146	51	0.81	0.135	0.7
0.12	0.12	4	2274	1083	65	1.63	0.136	1.1	0.18	0.06	4.5	6383	902	50	0.81	0.135	0.7
0.12	0.12	5	1906	1059	72	1.63	0.136	1.1	0.18	0.06	5	7539	1340	60	0.81	0.135	0.7
0.12	0.12	7	2054	1414	82	1.63	0.136	1.1	0.18	0.06	6	8293	1592	64	0.81	0.135	0.7
0.06	0.015	0.5	8476	162	9	0.21	0.140	2.3									
0.06	0.015	1	8922	326	18	0.21	0.140	2.3									
0.06	0.015	1.5	10488	560	25	0.21	0.140	2.3									

C_{HgBr_2}, mol/l	$C_{NO_2C_6H_4CH_2HgBr}$, mol/l	Exchange time, h	A_{HgBr_2}, imp/min	$A_{NO_2C_6H_4CH_2HgBr}$, imp/min	F, %	Initial rate $R \cdot 10^3$, mol·l^{-1}·h^{-1}	$K_{NO_2C_6H_4CH_2HgBr}$, h^{-1}	K_2, l·mol^{-1}·h^{-1}	C_{HgBr_2}, mol/l	$C_{NO_2C_6H_4CH_2HgBr}$, mol/l	Exchange time, h	A_{HgBr_2}, imp/min	$A_{NO_2C_6H_4CH_2HgBr}$, imp/min	F, %	Initial rate $R \cdot 10^3$, mol·l^{-1}·h^{-1}	$K_{NO_2C_6H_4CH_2HgBr}$, h^{-1}	K_2, l·mol^{-1}·h^{-1}
0.06	0.015	2.5	9030	658	34	0.21	0.140	2.3									
0.06	0.015	4.5	9248	1183	56	0.21	0.140	2.3									
0.06	0.015	5	7842	1050	59	0.21	0.140	2.3									
0.06	0.015	7	8839	1436	70	0.21	0.140	2.3									
0.06	0.03	0.5	6529	233	10	0.46	0.154	2.6									
0.06	0.03	1	4781	330	19	0.46	0.154	2.6									
0.06	0.03	1.5	8904	825	25	0.46	0.154	2.6									
0.06	0.03	2	5875	838	37	0.46	0.154	2.6									
0.06	0.03	2.5	5462	933	44	0.46	0.154	2.6									
0.06	0.03	3	5626	1193	53	0.46	0.154	2.6									
0.06	0.03	3.5	4770	1127	58	0.46	0.154	2.6									
0.06	0.03	4	5089	1308	61	0.46	0.154	2.6									
0.06	0.03	5.5	4821	1578	74	0.46	0.154	2.6									
0.06	0.03	7	4728	1727	81	0.46	0.154	2.6									

···of the solution by means of a capillary and applied to strips of chromatographic paper 1.3 cm wide. The DMSO was evaporated from the paper in a stream of air heated to 40°, after which the paper was impregnated with a 10% solution of ethylene glycol in acetone. Chromatography was carried out with an octane—benzene mixture in a ratio of 1 : 4. The chromatograms were divided into equal parts, the activities of which were measured on a B-2 apparatus with an MST-17 counter. The degree of exchange was calculated from the formula:

$$F = \frac{A_{NO_2C_6H_4CH_2HgBr}}{A_{NO_2C_6H_4CH_2HgBr} + A_{HgBr_2}} \cdot \frac{C_{NO_2C_6H_4CH_2HgBr} + C_{HgBr_2}}{C_{NO_2C_6H_4CH_2HgBr}},$$

where C is the concentration in mol/l, and A is the activity in imp/min.

Table 1 gives experimental data* on the dependence of the degree of exchange on the concentration of the reagents at a temperature of 70°.

From the data of Table 1, for various equimolecular concentrations of mercuric bromide and the organomercury compound, a plot was constructed in the coordinates $-\lg(1-F)$–t (Fig. 1). As can be seen, the half-exchange period does not depend on

* The activities were measured in parallel in two samples; the error in measuring the exchange did not exceed 7% on average. Table 1 gives the data of one measurement.

Fig. 3. For determining the activation energy of the isotope-exchange reaction of n-$NO_2C_6H_4CH_2HgBr$ with $Hg^{203}Br_2$ in DMSO

Figure 2: Fig. 3. For determining the activation energy of the isotope-exchange reaction of n-$NO_2C_6H_4CH_2HgBr$ with $Hg^{203}Br_2$ in DMSO

concentrations and remains constant. It follows from this that the reaction has an overall order equal to 1.

On the basis of a study of the dependence of the reaction rate on the concentration of one of the components (the concentration of the other component being kept constant), the partial orders of the reaction were determined. Figure 2 gives the graphical dependence of the logarithm of the initial rate of the isotope-exchange reaction on the concentration of each of the components.

Fig. 3. For determining the activation energy of the isotope-exchange reaction of n-$NO_2C_6H_4CH_2HgBr$ with $Hg^{203}Br_2$ in DMSO

At a constant concentration of the organomercury compound, the initial reaction rate is practically independent of the concentration of mercuric bromide (straight line 2 is parallel to the abscissa axis, Fig. 2). However, at a constant concentration of mercuric bromide the initial reaction rate increases with increasing concentration of the organomercury compound, the tangent of the angle of inclination of straight line 1 being equal to unity. These data indicate that the reaction under study is of zero order with respect to mercuric bromide and of first order with respect to the organomercury compound, i.e., it is a monomolecular reaction. The first-order rate constants given in Table 1 remain quite constant, which is not observed for the second-order rate constants.

Table 2

Temp., °C	Exchange time, t, h	AH_2gBr_2, imp/min	$ANO_2C_6H_4CH_2HgBr$, imp/min	Extent of exchange, %	K_1, h^{-1}	lg K_1	Temp., °C	Exchange time, t, h	$AHgBr_2$, imp/min	$ANO_2C_6H_4CH_2HgBr$, imp/min	Extent of exchange, %	K_1, h^{-1}	lg K_1
40	2	3342	78	5	0.011	−1.97	60	0.5	3725	179	9	0.062	−1.21
40	5.5	2984	178	11	0.011	−1.97	60	1.5	3500	241	13	0.062	−1.21
40	10	3102	317	19	0.011	−1.97	60	2.5	3046	381	22	0.062	−1.21
40	21.5	2503	632	40	0.011	−1.97	60	3.5	2975	622	35	0.062	−1.21
40	15.5	2760	471	29	0.011	−1.97	60	5	2685	881	49	0.062	−1.21
40	23	2735	624	37	0.011	−1.97	60	9	2568	1290	67	0.062	−1.21
40	29	2191	641	45	0.011	−1.97	70	0.5	4904	321	12	0.136	−0.87
50	1.5	3739	141	7	0.026	−1.58	70	1.5	3369	659	33	0.136	−0.87
50	3	3097	176	11	0.026	−1.58	70	3	3000	1308	61	0.136	−0.87
50	5	3274	379	21	0.026	−1.58	70	4	2375	1205	67	0.136	−0.87
50	7.3	2519	514	34	0.026	−1.58	70	6	2236	1534	81	0.136	−0.87

Temp., °C	Exchange time, t, h	$A_{\mathrm{HgBr_2}}$, imp/min	$A_{\mathrm{NO_2C_6H_4HgBr}}$, imp/min	Extent of exchange, %	K_1, h^{-1}	$\lg K_1$	Temp., °C	Exchange time, t, h	$A_{\mathrm{HgBr_2}}$, imp/min	$A_{\mathrm{NO_2C_6H_4HgBr}}$, imp/min	Extent of exchange, %	K_1, h^{-1}	$\lg K_1$
50	10	2582	674	44	0.026	−1.58	70	7.7	2285	1793	88	0.136	−0.87
50	13	2193	750	51	0.026	−1.58							
50	16.5	2471	1005	58	0.026	−1.58							
50	20	2196	1113	67	0.026	−1.58							

Table 2 gives the dependence of the extent of exchange at temperatures of 40, 50, 60, and 70° and constant reagent concentrations of 0.06 mol/l. From these data a plot of the dependence

$$\lg K_1 = f(1/T)$$

was constructed (Fig. 3), from which the parameters of the Arrhenius equation were calculated:

$$E = 18 \pm 1 \text{ kcal/mol}, \qquad \lg A = 10.65$$

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