



Soviet-era science, translated into English

CHEMISTRY

V. A. KALYAVIN, T. A. SMOLINA, Corresponding Member of
the Academy of Sciences of the USSR O. A. REUTOV

1964

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196401.08183>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

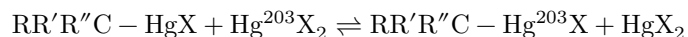
CHEMISTRY

V. A. KALYAVIN, T. A. SMOLINA, Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV

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

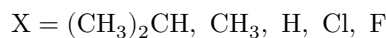
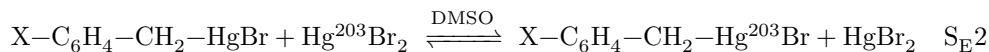
In the last decade interest has sharply increased in the study of electrophilic substitution reactions. It is obvious that the regularities obtained in this way may directly or indirectly contribute to the elucidation of a number of general questions concerning mechanisms of substitution reactions at 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:

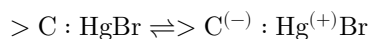


one of us, together with co-workers^(1,2), succeeded for the first time in carrying out an S_E1 -reaction (first kinetic order with respect to the organomercury compound and zero order with respect to mercuric halide) for the case of the ethyl ester of α -bromomercuriphenylacetic acid, using solvents 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

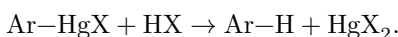
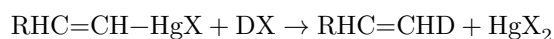


i.e., just as when quinoline is used as the solvent ⁽⁴⁾. Obviously, despite the high ionizing power of DMSO, in the present case it is insufficient to ionize the strong C–Hg bond with formation of an ion pair:



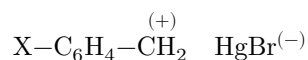
It is natural to assume that the probability of an S_E1 -mechanism for the reaction under consideration in DMSO should increase in the case where the carbanion formed as a result of ionization possesses greater stability owing to delocalization of the negative charge, for example.

* 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:



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

structural factors:



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.

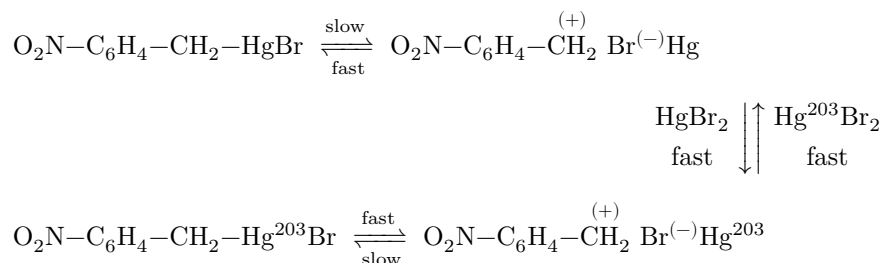
We studied the kinetics of isotopic exchange of *p*-nitrobenzylmercury bromide with radioactive mercuric bromide in DMSO. As we had assumed, the reaction has an overall first order (first order with respect to the organomercury compound and zero order with respect to mercuric bromide).

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



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 $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}$ with $\text{Hg}^{203}\text{Br}_2$ 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.

$$1-\lg R = f(C_{\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}}); 2-\lg R = f(C_{\text{HgBr}_2})$$

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

$\text{C}_7\text{H}_6\text{BrHgNO}_2$. 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

										Initial													Initial		
										Degree													Degree		
										of R													of R		
										ex- 10^3 ,													ex- 10^3 ,		
										Exchange													Exchange		
										change													change		
										mol · l ⁻¹ · h ⁻¹													mol · l ⁻¹ · h ⁻¹		
C_{HgBr_2}	C_{NO_2}	$C_{\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}}$	time	A_{HgBr_2}	A_{NO_2}	$A_{\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}}$	F_{HgBr_2}	F_{NO_2}	$F_{\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}}$	K_1	K_2	K_3	C_{HgBr_2}	C_{NO_2}	$C_{\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}}$	time	A_{HgBr_2}	A_{NO_2}	$A_{\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}}$	F_{HgBr_2}	F_{NO_2}	$F_{\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}}$	K_1	K_2	K_3
mol/h	mol/h	mol/h	h	imp/imp	imp/imp	imp/imp	in	in	in	h ⁻¹	h ⁻¹	h ⁻¹	mol	mol	mol	h	imp/imp	imp/imp	imp/imp	in	in	in	h ⁻¹	h ⁻¹	h ⁻¹
0.03	0.03	0.5	3349147	8	0.41	0.136	1.5	0.06	0.12	0.5	5518107724	0.71	0.143	2.3											
0.03	0.03	1	3098310	18	0.41	0.136	1.5	0.06	0.12	1	4264152039	0.71	0.143	2.3											
0.03	0.03	2	2832740	41	0.41	0.136	1.5	0.06	0.12	1.5	2650132550	0.71	0.143	2.3											
0.03	0.03	3.5	2474107261		0.41	0.136	1.5	0.06	0.12	2.5	1873132162	0.71	0.143	2.3											
0.03	0.03	5.5	2306146578		0.41	0.136	1.5	0.06	0.12	3.5	1920201277	0.71	0.143	2.3											
0.03	0.03	8	1886146688		0.41	0.136	1.5																		
0.06	0.06	0.0	431273	3	0.82	0.130	2.3	0.03	0.06	0.5	1382123	12	0.75	0.124	1.1										
0.06	0.06	0.5	4904321	12	0.82	0.130	2.3	0.03	0.06	1	1333268	25	0.75	0.124	1.1										
0.06	0.06	1.5	3369659	33	0.82	0.130	2.3	0.03	0.06	1.5	2209738	38	0.75	0.124	1.1										
0.06	0.06	3	3000130861		0.82	0.130	2.3	0.03	0.06	2	1895111952		0.75	0.124	1.1										
0.06	0.06	4	2375120567		0.82	0.130	2.3	0.03	0.06	2.5	1727118161		0.75	0.124	1.1										
0.06	0.06	6	2236153481		0.82	0.130	2.3	0.03	0.06	3	1613151673		0.75	0.124	1.1										
0.06	0.06	7.7	2285179388		0.82	0.130	2.3	0.03	0.06	4	1466159578		0.75	0.124	1.1										
								0.03	0.06	4.5	1408169282		0.75	0.124	1.1										
								0.03	0.06	5	1230152883		0.75	0.124	1.1										
0.09	0.09	0.5	4527284	12	1.22	0.136	1.5	0.12	0.06	0.5	6925195	8	0.79	0.132	1.1										
0.09	0.09	1.5	3367685	34	1.22	0.136	1.5	0.12	0.06	1	6516343	15	0.79	0.132	1.1										
0.09	0.09	2	3247889	43	1.22	0.136	1.5	0.12	0.06	1.5	6301572	25	0.79	0.132	1.1										
0.09	0.09	3	3180123756		1.22	0.136	1.5	0.12	0.06	2	6144735	32	0.79	0.132	1.1										
0.09	0.09	4.5	2911156970		1.22	0.136	1.5	0.12	0.06	2.5	6067920	39	0.79	0.132	1.1										
0.09	0.09	6	2650169678		1.22	0.136	1.5	0.12	0.06	3	5878109847		0.79	0.132	1.1										
0.09	0.09	7	2707207487		1.22	0.136	1.5	0.12	0.06	3.5	4464987	54	0.79	0.132	1.1										
								0.12	0.06	4.5	5117123358		0.79	0.132	1.1										
								0.12	0.06	5	4595117061		0.79	0.132	1.1										
								0.12	0.06	5	4859129663		0.79	0.132	1.1										
0.12	0.12	0.0	269230	2	1.63	0.136	1.1	0.18	0.06	0.5	1000042	9	0.81	0.130	0.7										
0.12	0.12	0.5	156494	11	1.63	0.136	1.1	0.18	0.06	1	9496364	15	0.81	0.130	0.7										
0.12	0.12	1	2875409	25	1.63	0.136	1.1	0.18	0.06	1.5	8800565	24	0.81	0.130	0.7										
0.12	0.12	1.5	3142659	35	1.63	0.136	1.1	0.18	0.06	2	8156672	30	0.81	0.130	0.7										
0.12	0.12	2	2267587	41	1.63	0.136	1.1	0.18	0.06	2.5	7970735	34	0.81	0.130	0.7										
0.12	0.12	2.5	2862987	51	1.63	0.136	1.1	0.18	0.06	3.5	7763976	45	0.81	0.130	0.7										
0.12	0.12	3	1906826	58	1.63	0.136	1.1	0.18	0.06	4	7907114651		0.81	0.130	0.7										
0.12	0.12	4	2274108365		1.63	0.136	1.1	0.18	0.06	4.5	6383902	50	0.81	0.130	0.7										
0.12	0.12	5	1906105972		1.63	0.136	1.1	0.18	0.06	5	7539134060		0.81	0.130	0.7										
0.12	0.12	7	2054141482		1.63	0.136	1.1	0.18	0.06	6	8293159264		0.81	0.130	0.7										
0.06	0.015	0.5	8476162	9	0.21	0.140	2.3																		
0.06	0.015	1	8922326	18	0.21	0.140	2.3																		
0.06	0.015	1.5	1048860	25	0.21	0.140	2.3																		

		Initial					Initial						
		Degree					Degree						
		of R.					of R.						
		ex- 10 ³ , K ₂ ,					ex- 10 ³ , K ₂ ,						
		change					change						
C _{HgBr₂}	C _{NO₂C₆H₄CH₂HgBr}	time	A _{HgBr₂}	A _{NO₂C₆H₄CH₂HgBr}	F	l ⁻¹ · K ₂	C _{HgBr₂}	C _{NO₂C₆H₄CH₂HgBr}	time	A _{HgBr₂}	A _{NO₂C₆H₄CH₂HgBr}	F	l ⁻¹ · K ₂
mol/h	mol/h	h	imp/min	imp/min	h ⁻¹	h ⁻¹	mol/h	mol/h	h	imp/min	imp/min	h ⁻¹	h ⁻¹
0.06	0.015	2.5	9030658	34	0.21	0.14	0.3						
0.06	0.015	4.5	9248118356	0.21	0.14	0.3							
0.06	0.0155	7842105059	0.21	0.14	0.3								
0.06	0.0157	8839143670	0.21	0.14	0.3								
0.06	0.03	0.5	6529233	10	0.46	0.15	2.6						
0.06	0.03	1	4781330	19	0.46	0.15	2.6						
0.06	0.03	1.5	8904825	25	0.46	0.15	2.6						
0.06	0.03	2	5875838	37	0.46	0.15	2.6						
0.06	0.03	2.5	5462933	44	0.46	0.15	2.6						
0.06	0.03	3	5626119353	0.46	0.15	2.6							
0.06	0.03	3.5	4770112758	0.46	0.15	2.6							
0.06	0.03	4	5089130861	0.46	0.15	2.6							
0.06	0.03	5.5	4821157874	0.46	0.15	2.6							
0.06	0.03	7	4728172781	0.46	0.15	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 $n\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}$ with $\text{Hg}^{203}\text{Br}_2$ in DMSO

Figure 2: Fig. 3. For determining the activation energy of the isotope-exchange reaction of $n\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}$ with $\text{Hg}^{203}\text{Br}_2$ 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 $n\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}$ with $\text{Hg}^{203}\text{Br}_2$ 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., t , °C	Exchange time, h	Extent of ex- change					Temp., t , °C	Exchange time, h	Extent of ex- change				
		AHgBr	$\text{A}(\text{NO}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}$	Cl_2	Cl_2	Cl_2			AHgBr	$\text{A}(\text{NO}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{HgBr}$	Cl_2	Cl_2	Cl_2
		imp/mmp	imp/mmp	imp/mmp	h^{-1}	$\lg K_1$			imp/mmp	imp/mmp	imp/mmp	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	t, h	Extent of exchange					Temp., °C	t, h	Extent of exchange				
		AH ₂ g	Br ₂	Cl ₂	HgCl ₂	HgBr ₂			AH ₂ g	Br ₂	Cl ₂	HgCl ₂	HgBr ₂
		imp/mil	imp/mil	%	h ⁻¹	lg K ₁			imp/mil	imp/mil	%	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:

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

Moscow State University
named after M. V. Lomonosov

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
31 I 1964

CITED LITERATURE

1. O. A. Reutov, V. I. Sokolov, I. P. Beletskaya, DAN, **136**, No. 3, 631 (1961).
2. O. A. Reutov, B. P. Fisher et al., Izv. AN SSSR, OKhN, 1963, 970.
3. V. A. Kalyavin, T. A. Smolina, O. A. Reutov, DAN, **155**, No. 3 (1964).
4. O. A. Reutov, T. A. Smolina, V. A. Kalyavin, DAN, **139**, No. 2, 389 (1961); **35**, 119 (1962).
5. O. A. Reutov, V. I. Sokolov, DAN, **136**, No. 2, 366 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.