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Abstract

Full Text

Chemistry

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ON THE MECHANISM OF THE ISOTOPIC EXCHANGE REACTION OF DIALKYLMERCURY WITH ALKYLMERCURY HALIDES

The present article describes a new isotopic-exchange reaction of alkylmercury compounds:

$$R_2Hg + RHg^{203}X \rightleftarrows R_2Hg^{203} + RHgX,$$

$$\left(R = (CH_3)_2CHCH_2CH_2\overset{*}{C}HCH_3,\ X = Br\right)$$

As starting substances we used optically active 5-bromomercuri-2-methylhexane and bis-(2-methylhexyl-5)-mercury ([1]).

The exchange reaction was carried out in absolute alcohol at 60°, in the dark, with equimolecular concentrations of the reagents ($0.05\,M$). Samples of the reaction solution (10–12 ml) were diluted with petroleum ether and washed several times with water to remove the alcohol. The mixture of reagents in petroleum ether was separated on an Al_2O_3 column. Dialkylmercury was eluted with petroleum ether, and alkylmercury bromide with diethyl ether.

Dialkylmercury was converted by the action of $HgBr_2$ into alkylmercury bromide. In the latter, the radioactivity and, at the same time, the specific rotation were determined. During separation and purification of the substances their angle of rotation does not change.

In experiment No. 1, optically active alkyl bromide labeled with Hg^{203} and racemic dialkylmercury were used. As the reaction proceeded, a distribution of optical activity between RHgBr and R_2Hg was observed. As the characteristic of the optical activity of dialkylmercury (α_{R_2Hg}), twice the angle of rotation of RHgBr, obtained from R_2Hg by the action of $HgBr_2$, was taken* (for RHgBr, $[\alpha]_D^{20} = \alpha_{RHgBr}$, $\alpha_{R_2Hg} = 2\alpha_{RHgBr}$).

All measurements of angles were made in absolute alcohol. In experiment No. 2, racemic RHgBr and optically active dialkylmercury with an angle of rotation $[\alpha]_D^{20} = -21.7°$ ($\alpha_{R_2Hg} = -31.4°$) were taken. The amount of optically active radicals in the reaction mixture was monitored by determining α_{RHgBr} and $\alpha_{\mathrm{R_2Hg}}$ for RHgBr and R_2Hg isolated from each sample. In both the first and the second experiments, the sum $\alpha_{\mathrm{RHgBr}} + \alpha_{\mathrm{R_2Hg}}$ remained constant from the beginning to the end of the reaction (within the experimental error of ±4%).

In experiment No. 2, the angle of rotation of the reaction mixture increased with time, since the active radicals passed from dialkylmercury into alkylmercury bromide, which has a larger specific angle of rotation. From these data, $\alpha_{\mathrm{R_2Hg}}$ and $(\alpha_{\mathrm{RHgBr}} + \alpha_{\mathrm{R_2Hg}})$ were calculated, agreeing well with the values obtained after separation of the mixture.

The results of the experiments are given in Tables 1 and 2.

From the data presented in Tables 1 and 2, it follows first of all that the isotopic-exchange reaction under consideration proceeds with strict preservation— by inversion of the configuration at the asymmetric carbon atom: the sum $\alpha_{\mathrm{RHgBr}} + \alpha_{\mathrm{R_2Hg}}$ remains constant in the course of the reaction.

Table 1

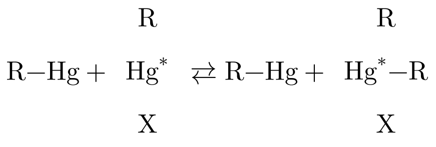
Experiment No. 1*. Data on isotopic exchange and radical exchange

Time, h	Isotopic exchange, %	$\alpha_{\mathrm{R_2Hg}}$	α_{RHgBr}	$\alpha_{\mathrm{RHgBr}} + \alpha_{\mathrm{R_2Hg}}$	Mean sum $\alpha_{\mathrm{RHgBr}} + \alpha_{\mathrm{R_2Hg}}$
3	60.0	−7.6 ± 0.5**	−15.4±0.3	−23.0±0.8	
5	70.0	−8.3 ± 1.2	−12.2±0.2	−20.5±1.4	21.6 ± 0.9
10	97.0	−10.6±0.2	−10.6±0.2	−21.2±0.4	

* The reagents were dissolved together while being heated; therefore the initial rate was increased.
** The accuracy was calculated from a measurement error of ±0.005°.

Let us now consider possible schemes for the reaction mechanism:

I. Exchange of R for X (R ⇄ X)



$$\mathrm{R{-}Hg} + \overset{\mathrm{R}}{\underset{\mathrm{X}}{\mathrm{Hg}^*}} \rightleftarrows \mathrm{R{-}Hg} + \overset{\mathrm{R}}{\underset{\mathrm{X}}{\mathrm{Hg}^*}}\mathrm{{-}R}$$

II. Exchange of R for R (R ⇄ R)

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* The reaction of Alk_2Hg with $HgBr_2$ proceeds with complete retention of configuration at the asymmetric carbon atom ([2,3]).

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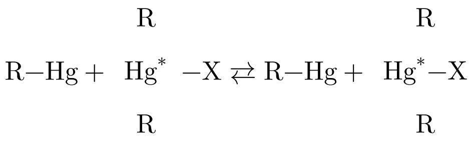

$$R{-}Hg + \underset{R}{\overset{R}{Hg^*}}{-}X \rightleftarrows \underset{R}{\overset{R}{R{-}Hg}} + Hg^*{-}X$$

III. Exchange of Hg for Hg^* ($Hg \rightleftarrows Hg^*$).

Table 2

Time, h	α_{RHgBr}	α_{R_2Hg}	$\alpha_{RHgBr}+\alpha_{R_2Hg}$	Reaction-mixture angle	Radical exchange, %	$\ln(1-F)$	$V \cdot 10^3$, mol/l/h	$V \cdot 10^3$, mean
2	−3.2± 0.2	−28.8± 0.2	−32.0± 0.4		21.2	0.103	4.0	
3	−3.1± 0.2	−27.6± 0.4	−30.7± 0.6		32.7	0.172	4.4	
4	−3.9± 0.3	−26.6± 0.4	−30.5± 0.7	−0.452	42.4	0.240	4.6	
	–		−30.6*					4.4 ± 0.3
5	–	−25.8± 0.4	–	–	50.0	0.301	4.6	
6	−4.8± 0.3	−24.8± 0.4	−29.6± 0.7	−0.459	59.6	0.394	5.0	
			−30.4*					
15**	−10.8*	−20.2± 0.5	−31.0*	−0.479	104			

* The angle was calculated from the angle of rotation of the reaction mixture.
** The mixture was kept for a further 14 h at room temperature.

In this case both radicals in R_2Hg, so to speak, "slide" from their mercury atom onto the radioactive mercury atom, while R and X simultaneously "slide" from the radioactive mercury atom onto the mercury atom that formerly belonged to the R_2Hg molecule.

IV. A free-radical chain mechanism.

V. Isotopic exchange complicated by the presence of the equilibrium

$$2RHgX \rightleftarrows R_2Hg + HgX_2$$

Scheme I agrees with our experimental results; schemes II—V contradict them.

Table 3

Experiment No. 2. Growth of isotopic exchange

	Time, h	Time, h	Time, h	Time, h	Time, h
	2	3	4	5	6
Isotopic exchange, %	33.0	48.5	54.0	65.0	69.5
$-\ln(1-F)$	0.174	0.287	0.338	0.426	0.516
$V \cdot 10^3$, mol/l • h	5.00	5.50	4.85	4.90	4.95
$V \cdot 10^3$, average		5.0 ± 0.2			

The reaction does not proceed with the participation of free radicals as kinetically independent particles (scheme IV), since complete preservation of the stereochemical configuration is observed. If the reaction followed scheme III, then it would not be accompanied by redistribution of optical activity between RHgX and R_2Hg.

The considerations given below show that the isotopic exchange under consideration is complicated neither by equilibrium (a) of scheme V, nor by parallel reactions proceeding according to schemes II and III.

Fig. 1

The isotopic exchange obeys the equation:

$$-\ln(1-F) = \frac{A+B}{AB} Vt, \tag{1}$$

where F is the degree of exchange, A and B are the concentrations of the initial substances, V is the exchange-rate constant, and t is time.

Redistribution of optically active radicals in the reaction:

$$R_2Hg + R^*HgBr \rightleftharpoons RHgR^* + RHgBr,$$

where R^* is an optically active radical, is in a certain sense analogous to isotopic exchange. Owing to the chemical indistinguishability of the radicals, at a certain point in time an equilibrium is established, characterized by the fact that RHgBr will contain 1/3 of the initial amount of optically active radicals, and dialkylmercury 2/3; after this, redistribution continues at the same rate, but already under conditions of "optical equilibrium."

Therefore, for the process of radical exchange one may also write an equation expressing the exponential dependence of the degree of exchange on time:

$$-\ln(1-F') = \frac{2A+B}{2AB} V't, \tag{2}$$

where F' is the degree of exchange by radicals, $F' = \dfrac{\alpha_t}{\alpha_\infty}$; α_t is the rotation angle of RHgX at time t, α_∞ is the rotation angle of RHgX after equilibrium has been reached, A is the concentration of R_2Hg; it is doubled, since there are two radicals; B is the concentration of RHgX, V' is the rate constant, and t is time.

The experimentally obtained exponential dependence of the degree of exchange of optically active radicals on time (experiment No. 2) is shown in Fig. 1, II.

The increase in the degree of isotopic exchange is shown on the same graph (straight line I) and in Table 3.

It is obvious that, according to scheme I, the exchange between mercury and radicals must occur in a single act:

$$\mathrm{R^*Hg^{203}X + RHgR \rightleftarrows R^*Hg^{203}R + RHgX}$$

$$\mathrm{R^*HgR + RHg^{203}X \rightleftarrows R_2Hg^{203} + R^*HgX,}$$

therefore the exchange rates V and V' from equations (1) and (2) may be equated: $V = V'$. If the reaction under consideration proceeded not only as a result of exchange of R for X, but also (at least in part) as a result of exchange of R for R (scheme II), then the rate of radical exchange should exceed the rate of isotopic exchange of mercury atoms ($V' > V$). If the slipping mechanism (scheme III) played even a partial role in the reaction, then $V' < V$.

Table 4

Comparison of the measured angles of rotation and the angles calculated from isotopic exchange

	3*	5*	2	3	4	5	6
Measured α_{R_2Hg}	−7.6°	−8.11°	−28.8°	−27.6°	−26.6°	−25.8°	−24.8°
Calculated α_{R_2Hg}	−7.6°	−8.3°	−28.3°	−27.0°	−26.4°	−25.6°	−24.9°
Relative deviation	0%	2.5%	1.8%	2.2%	0.8%	0.8%	0.4%

* Data from experiment No. 1; the remaining data are from experiment No. 2.

It is also extremely unlikely that the reaction would proceed simultaneously according to schemes II and III while maintaining equality of the rates for these different processes.

In a reaction according to scheme V,

$$2R^{*}Hg^{203}X \rightleftarrows R_2^{*}Hg^{203} + Hg^{203}X_2,$$

$$R_2Hg + Hg^{203}X_2 \rightleftarrows RHgX + RHg^{203}X,$$

each act of exchange by a mercury atom must be accompanied by exchange of two optically active radicals (i.e. $V' > V$):

$$2R^{*}Hg^{203}X + R_2Hg \rightleftarrows R_2^{*}Hg^{203} + RHg^{203}X + RHgX.$$

Our experiments have established the equality of V and V' (Tables 2 and 3) within experimental error. Thus it has been proved that the reaction proceeds only according to scheme I. Bearing in mind that $V = V'$, one can derive an equation relating the degree of isotopic exchange F and the exchange of radicals F'. Dividing (1) by (2), we obtain:

$$\ln(1 - F') = \frac{2A + B}{2(A + B)} \ln(1 - F). \tag{3}$$

Table 4 gives the angles of rotation (α_{R_2Hg}) calculated from the degrees of isotopic exchange by formula (3) (the deviations from the experimental value are no more than 2.5%).

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

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