Corresponding Member of the USSR Academy of Sciences O. A. REUTOV, T. P. KARPOV, E. V. UGLOVA, and V. A. MALYANOV

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

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the USSR Academy of Sciences O. A. REUTOV, T. P. KARPOV, E. V. UGLOVA, and V. A. MALYANOV

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:

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

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

Optically active 5-bromomercuri-2-methylhexane and bis-(2-methylhexyl-5)-mercury (^{1}) were used as starting substances.

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 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. For the latter, the radioactivity and, simultaneously, 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, 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 carried out 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 experiment, 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 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, which agree 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 preserv—

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

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 under heating; therefore the initial rate was increased.
** The accuracy was calculated from an error of measurement of ±0.005°.

change in configuration at the asymmetric carbon atom: the sum $\alpha_{\mathrm{RHgBr}}+\alpha_{\mathrm{R_2Hg}}$ remains constant in the course of the reaction.

Let us now consider the possible schemes for the reaction mechanism:

I. Exchange of R for X (R ⇄ X)

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

II. Exchange of R for R (R ⇄ R)

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

III. Exchange of Hg for *Hg (Hg ⇄ *Hg).

Table 2

Time, h	α_{RHgBr}	α_{R_2Hg}	$\alpha_{RHgBr}+\alpha_{R_2Hg}$	Angle of reaction mixture	Exchange, rad.-chem., %	$\ln(1-F)$	$V\cdot 10^3$, 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	
4	–	–	−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	
6			−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 another 14 h at room temperature.

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

IV. 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. Increase in isotope exchange

	Time, h	Time, h	Time, h	Time, h	Time, h
	2	3	4	5	6
Isotope exchange, %	33.0	48.5	54.0	65.0	69.5

Fig. 1

Figure 1: Fig. 1

	Time, h	Time, h	Time, h	Time, h	Time, h
$-\ln(1-F)$	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 occur with the participation of free radicals as kinetically independent particles (scheme IV), since complete preservation of the stereochemical configuration is observed. If the reaction proceeded according to scheme III, it would not be accompanied by redistribution of optical activity between RHgX and R_2Hg.

The considerations given below show that the isotope exchange under consideration is not complicated either by equilibrium (a) of scheme V or by parallel reactions proceeding according to schemes II and III.

Fig. 1

Isotope 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 starting substances, V is the constant exchange rate, and t is time.

Redistribution of optically active radicals in the reaction:

$$\mathrm{R_2Hg + R^*HgBr \rightleftarrows RHgR^* + RHgBr},$$

where R^* is an optically active radical, is in a certain sense analogous to isotope exchange. Owing to the chemical indistinguishability of the radicals, at a certain moment 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, the 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 radical exchange, $F' = \dfrac{\alpha_t}{\alpha_\infty}$; α_t is the angle of RHgX at time t, α_∞ is the 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 isotope exchange is shown on the same graph (line I) and in Table 3.

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

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

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

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

Table 4

Comparison of the measured angles of rotation and the angles calculated from isotope 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 rates for these heterogeneous processes.

For a reaction according to scheme V

$$2R^*Hg^{203}X \rightleftarrows {}^*R_2Hg^{203} + Hg^{203}X_2,$$

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

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 isotope exchange F and radical exchange 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 isotope exchange by formula (3) (deviations from the experimental value are no more than 2.5%).

Moscow State University
named after M. V. Lomonosov

Received
27 V 1960

REFERENCES

1. O. A. Reutov, E. V. Uglova, *Izv. AN SSSR, OKhN*, 1959, 757.
2. N. V. Chapman, E. D. Hughes, C. K. Ingold, *J. Chem. Soc.*, 1959, 2530.
3. O. A. Reutov, E. V. Uglova, *Izv. AN SSSR, OKhN*, 1959, 1691.

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

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