Tetrahedron Letters No. 19, pp 6-15, 1960. Pergamon Press Ltd. Printed in Great Britain

THE MECHANISM OF ISOTOPE EXCHANGE REACTIONS OF DIALKYLMERCURY AND ALKYLMERCURIC HALIDES[1]

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(Received 13 July 1960)

IN the course of systematic investigation of isotope exchange reactions of organomercuric compounds one of the present authors and his coworkers[2-6] have described the following types of reactions:

$$\mathrm{RHgX} + {}^{203}\mathrm{Hg} \rightleftharpoons \mathrm{R}^{203}\mathrm{HgX} + \mathrm{Hg} \qquad \text{(ref. 2)}$$

$$\mathrm{R_2Hg} + {}^{203}\mathrm{Hg} \rightleftharpoons \mathrm{R_2}{}^{203}\mathrm{Hg} + \mathrm{Hg} \qquad \text{(ref. 3)}$$

$$\mathrm{RHgX} + {}^{203}\mathrm{HgX_2} \rightleftharpoons \mathrm{R}^{203}\mathrm{HgX} + \mathrm{HgX_2} \qquad \text{(ref. 4)}$$

$$\mathrm{RHgX} + \mathrm{R'}^{203}\mathrm{HgX} \rightleftharpoons \mathrm{R}^{203}\mathrm{HgX} + \mathrm{R'HgX} \qquad \text{(ref. 5)}$$

$$\mathrm{R_2Hg} + \mathrm{R'_2}{}^{203}\mathrm{Hg} \rightleftharpoons \mathrm{R_2}{}^{203}\mathrm{Hg} + \mathrm{R'_2Hg} \qquad \text{(ref. 6)}$$

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[1] Translated by A. L. Pumpiansky, Moscow.

[2] O.A. Reutov and G.M. Ostapchuk, *Zh. Obschei Khim.* **29**, 1614 (1959).

[3] O.A. Reutov and G.M. Ostapchuk, *Dokl. Akad. Nauk SSSR* **117**, 826 (1957); O.A. Reutov, *Izv. Akad. Nauk SSSR, Otdel. chim. nauk* 684 (1958).

[4] O.A. Reutov, T.A. Smolina, Chang Tsei U and Ju.P. Bubnov, *Dokl. Visshei Shkoly* No. 2, 324 (1958); O.A. Reutov, P. Knoll and Chang Tsei U, *Dokl. Akad. Nauk SSSR* **120**, 1052 (1958).

[5] O.A. Reutov, *Angew. Chem.* No. 6, 198 (1960).

[6] O.A. Reutov, T.A. Smolina and Vang Hoon Hoo, *Izv. Akad. Nauk SSSR, Otdel. chim. nauk* 559 (1959).

Now we report on a novel isotope exchange reaction of alkylmercuric compounds:

$$R_2Hg \quad + \quad R^{203}HgX \quad \rightleftharpoons \quad R_2{}^{203}Hg \quad + \quad RHgX$$

$$[R = (CH_3)_2\ CHCH_2CH_2\underset{|}{\overset{*}{C}}HCH_3, \quad X = Br]$$

Optically active 5-bromomercuri-2-methyl hexane and bis(2-methylhexyl-5) mercury, obtained previously, were used as starting compounds.[7] Dialkylmercury was purified by distillation at 1.10^{-4} mm and 35-40°. (Found: C, 41.85, 41.88; H, 7.63, 7.61; Hg, 50.04, 50.06%. $C_{14}H_{30}H_9$ requires C, 42.21; H, 7.58; Hg, 50.2%.)

The exchange was carried out in absolute alcohol at 60° in the dark at an equimolecular concentration of reagents (0.05 mole). The reaction mixture samples (10-12 cm^3) were diluted with petroleum ether and repeatedly washed with water to remove alcohol.

The mixture of reagents in petroleum ether was separated through a column with Al_2O_3, dialkylmercury eluated with petroleum ether and alkylmercuric bromide with diethyl ether followed by colour reaction with dithizone Dialkylmercury was converted under the action of $HgBr_2$ into alkylmercuric bromide. The radioactivity and specific rotation of the latter was then estimated. Special experiments enabled us to determine that separation and purification did not affect the angle of rotation of the compounds. Labelled alkylmercuric bromide $R^{203}HgX$ was obtained by treating dialkylmercury with $^{203}HgBr_2$. Optically active alkylmercuric bromide, labelled with ^{203}Hg, and racemic dialkylmercury were used in run 1. As the reaction proceeded a distribution of optical activity between RHgX and R_2Hg was observed. A

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[7] O.A. Reutov and E.V. Uglova, Izv. Akad. Nauk SSSR, Otdel. chim. nauk 757 (1959).

double angle of rotation of RHgBr obtained from R_2Hg under the action of $HgBr_2$ was taken as a characteristic of the optical activity of dialkylmercury (α_{R_2Hg}).[8] RHgBr had $[\alpha]_D^{20} = \alpha_{RHgBr}$, $\alpha_{R_2Hg} = 2\alpha_{RHgBr}$.

The angles were all taken in absolute alcohol. Racemic RHgBr was used in run 2, together with optically active dialkylmercury having the angle of rotation $[\alpha]_D^{20} = -21.7^\circ$ $(\alpha_{R_2Hg} = -31.4^\circ)$ and produced by treating active alkylmercuric bromide with racemic Grignard reagent:

$$\overset{*}{R}HgBr + RMgX \rightleftharpoons \overset{*}{R}HgR$$

TABLE 1

Run 1: Isotope Exchange and Radical Exchange Data[a]

Time (hr)	Isotope exchange (%)	α_{R_2Hg}	α_{RHgX}	$\alpha_{R_2Hg} + \alpha_{RHgX}$	Average sum
3	60.0	-7.6 ± 0.5[b]	-15.4 ± 0.3	-23.0 ± 0.8	21.6 ± 0.9
5	70.0	-8.3 ± 1.2	-12.2 ± 0.2	-20.5 ± 1.4	
10	97.0	-10.6 ± 0.2	-10.6 ± 0.2	-21.2 ± 0.4	

[a] As the reagents dissolved together on heating, the rate of exchange was at first elevated.

[b] Precision was calculated in terms of each measurement accuracy which was about ± 0.005°.

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[8] Reaction of Alk_2Hg and $HgBr_2$ proceeds with complete retention of configuration at asymmetric carbon.[9,10]

[9] H. B. Charman, E.D. Hughes and C.K. Ingold, J. Chem. Soc. 2530 (1959).

[10] O.A. Reutov and E.V. Uglova, Izv. Akad. Nauk SSSR, Otdel. khim. nauk 1691 (1959).

TABLE 2

Run 2: Radical Exchange Data

Time (hr)	α RHgBr	α R_2Hg	α RHgBr + α R_2Hg	Angle of the reaction mixture=1	Radical exchange (%)	ln (1-F')	V!10^3 mole/ 1 hr	V!10^3 mean
I	II	III	IV	V	VI	VII	VIII	IX
2	-3.2±0.2	-28.8±0.2	-32.0±0.4		21.2	0.103	4.0	4.7±0.3
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 [a]					
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 [a]					
15	-10.8 [a]	-20.2±0.5	-31.0 [a]	-0.479	104			

[a] The angle was calculated from the angle of rotation of reaction mixture.

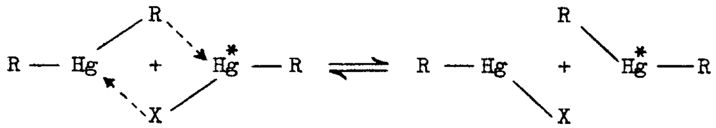
The number of optically active radicals in the reaction mixture was checked by determining α_{RHgBr} and α_{R_2Hg} for RHgBr and R_2Hg obtained from each sample. In both runs the sum of α_{RHgBr} and α_{R_2Hg} remained constant over the whole reaction (within the experimental error of ± 4 per cent).

In run 2 we also estimated the angle of rotation of the reaction mixture. This increased with time because the active radicals migrated from dialkylmercury to alkylmercuric bromide which has a greater specific angle of rotation. From these values we calculated α_{RHgBr} and $(\alpha_{RHgBr} + \alpha_{R_2Hg})$ which proved to be in good agreement with values obtained after the separation of the mixture.

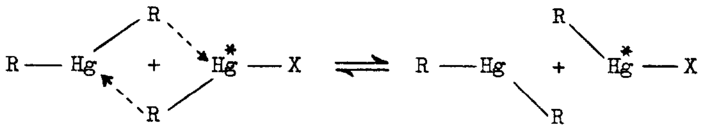
From the data listed in Tables 1 and 2 it can be seen that the isotope exchange reaction under consideration proceeds with strict retention of configuration at asymmetric carbon, the sum of $\alpha_{RHgBr} \pm \alpha_{R_2Hg}$ remaining constant during the reaction.

Let us now consider the possible mechanisms of our reaction. They seem to be limited to the following five alternatives.

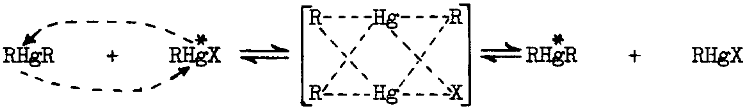
I Exchange of R to X ($R \rightleftharpoons X$)



II Exchange of R to R ($R \rightleftharpoons R$)

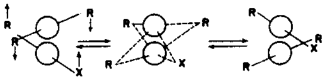


III Exchange of Hg to $\overset{*}{Hg}$



In this case both radicals in R_2Hg can be said to "slip" from their mercuric atom (the radioactive mercuric atom), with R and X simultaneously "slipping" from the radioactive mercuric atom (formerly belonging to the molecule R_2Hg[11]).

In the case of such a "slipping" the transition state appears to be represented by a bipyramidal complex such as:



with IV - a free radical chain mechanism and V the isotope exchange in the presence of equilibrium

$$2RHgX \rightleftharpoons R_2Hg + HgX_2$$

for example

$$\text{(a)}\ 2RH\overset{*}{g}X \rightleftharpoons R_2H\overset{*}{g} + H\overset{*}{g}X_2$$

$$\text{(b)}\ R_2Hg + H\overset{*}{g}X_2 \rightleftharpoons RH\overset{*}{g}X + RHgX$$

Scheme I is in agreement with our experimental data, Schemes II to V are not.

The reaction does not involve free radicals as kinetically independent particles (Scheme IV), the stereochemical configuration being thereby fully retained. Had the reaction followed Scheme III it would not have resulted in distribution of optical activity between RHgX and R_2Hg. The considerations below indicate that the isotope exchange in question proceeds with no equilibrium (Scheme Va) or with parallel reactions (Schemes II and III).

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[11] A simpler case of concurrent "slipping" of two radicals from one mercuric atom to another in the reaction $R_2Hg + {}^{203}Hg \rightleftharpoons R_2{}^{203}Hg + Hg$ can be considered as proven.[3]

The isotope exchange thus obeys the equation.

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

where F denotes the extent of exchange, A and B the concentration of starting substances, V the exchange rate constant and t the time.

Redistribution of optically active radicals in the reaction

$$R_2Hg + \overset{*}{R}HgX \rightleftharpoons \overset{*}{R}HgR + RHgX$$

with $\overset{*}{R}$ being an optically active radical, is in some way similar to isotope exchange. The radicals being chemically identical leads to the establishment at some particular moment of equilibrium that is characterized by RHgX containing 1/3 of the original amount of optically active radicals,with dialkylmercury accounting for the remaining 2/3; following this redistribution continues at the same rate but now in the condition of "optical equilibrium".

Hence, for the radical exchange process one can also write an equation expressing the exponential dependences of the extent of exchange on time such as

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

where F' is the extent of radical exchange, $F' = (\alpha_t)/(\alpha_\infty)$ with α_t and α_∞ denoting the angles of RHgX before and after equilibrium is reached; A is the concentration of R_2Hg that is doubled due to there being two radicals; B is the concentration of RHgX; V' is the constant exchange rate and t is the time.

Fig. 1. (curve II) shows the exponential dependence of the magnitude of exchange of optically active radicals on time determined experimentally (run 2).

The increase in isotope exchange is shown here (curve I) as well as in Table 3.

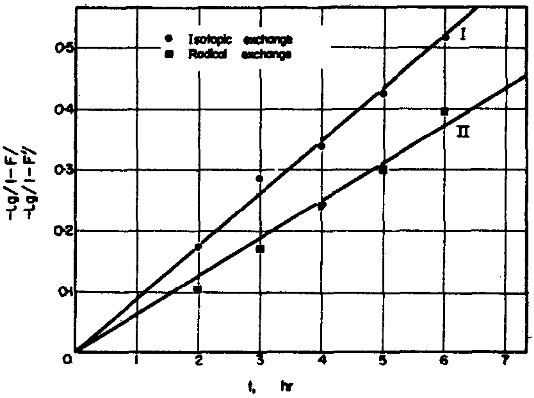

FIG. 1.

TABLE 3

Run 2: Increase in Isotope Exchange

Time (hr)	2	3	4	5	6
Isotope 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.10^3 mole/l.hr	5.00	5.50	4.85	4.90	4.95
V.10^3 (average)		5.0±0.2			

It is evident that according to Scheme I the exchange between mercury and radicals should take place in one step:

$$\overset{*}{R}{}^{203}Hg \vdots X + R \vdots HgR \rightleftharpoons \overset{*}{R}{}^{203}HgR + RHgX$$

$$\text{or} \quad \overset{*}{R}Hg \vdots R + R^{203}Hg \vdots X \rightleftharpoons R^{203}HgR + \overset{*}{R}HgX$$

Hence the exchange rates V and V' from equations (1) and (2) can be taken as equal, V=V'.

If, to some extent, exchange of R and R (Scheme II) and not only exchange of R and X had caused the reaction, the radical exchange rate should have exceeded that of the isotope exchange of mercuric atoms ($V' > V$). If the reaction had been at least partly affected by the mechanism of slipping (Scheme III), V should be greater than V'. It is also highly unlikely that the reaction might proceed simultaneously following Schemes I and II with these different processes running at equal rate. In the case of Scheme V

$$2\overset{*}{R}{}^{203}HgX \rightleftharpoons \overset{*}{R}_2{}^{203}Hg + {}^{203}HgX_2$$

$$R_2Hg + {}^{203}HgX_2 \rightleftharpoons RHgX + R^{203}HgX$$

each mercuric atom exchange must be accompanied by that of two optically active radicals (i.e. $V' > V$)

$$2\overset{*}{R}{}^{203}HgX + R_2Hg \rightleftharpoons \overset{*}{R}_2{}^{203}Hg + R^{203}HgX + RHgX$$

Our experiments have shown $V = V'$ (see Tables 2 and 3), within the limits of the experimental error. The reaction has thus been proved to follow Scheme 1 only.

Bearing in mind that $V = V'$, it is possible to write an equation to include both the magnitude of isotope exchange F and the radical exchange F'. For (1) and (2) one then obtains:

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

In Table 4 are given the angles of rotation (α_{R_2Hg}) calculated from the magnitude of isotope exchange in terms of equation (3) with deviations from the experimental value not exceeding 2.5 per cent.

To come to a definite conclusion with regard to the transition state in the reaction in question it is necessary to have some additional, primarily kinetic evidence, which is at present being accumulated.

TABLE 4

Comparative Data for the Measured Angles of Rotation

and Angles Calculated from Isotope Exchange

Time (hr)	3[a]	5[a]	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

[a] The data are taken from run 1, others from run 2.