# THE REDISTRIBUTION REACTION OF BIS-MERCURIALS

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#### ABSTRACT

The demetalation of diorganosubstituted mercury compounds is catalyzed by peroxides. When organomercuric salts are present this demetalation leads to formation of mercurous salt plus mercury. This latter combination has been found to be a catalyst for the redistribution reaction of bis-mercurials. It is suggested that all previously reported catalysts for this reaction operate by formation of the mercurous salt – mercury combination. Equilibration studies with this combination as catalyst indicate that random exchange is not general for the redistribution reaction of mercury compounds.

The equilibration of organic substituent groups among mixtures of bis-organolead, organotin, and organomercurials has been summarized (1) by Calingaert, who coined the name "redistribution reaction" originally for the equilibration of tetraalkyllead compounds in which the substituents were homologous or structurally isomeric (2). He applied the name also to the simpler equilibration of bis-mercurials (3).

$$2R' - Hg - R \rightleftharpoons R' - Hg - R' + R - Hg - R.$$

Obviously these reactions are, at most, "distributions"; the redundancy was unfortunate but at least it accentuated Calingaert's discovery that the "redistribution" was statistically random and unrelated to the structure of the substituent groups. Also, he demonstrated that the redistribution was catalyzed by metal halides and organometallic halides, including those related to the organometallic compounds that he was "redistributing".

Despite the mass of evidence relating to the redistribution reaction and its catalysis, we have found that for bis-mercurials it is quite erratic. For example, 4-cyclohexyl-mercuritoluene is recovered unchanged when it is treated in solvents such as methanol, petroleum ether, benzene, or dioxane with 1–5 mole % of the recommended (3) catalysts: boron fluoride etherate, aluminum chloride, magnesium bromide hydrate, zinc chloride, and cyclohexylmercuric chloride at room temperature. On the other hand, a moderately pure sample decomposes when heated without either solvent or any of the recommended catalysts, giving bis-4-tolylmercury. Likewise, for one operator, 2-butylmercuri-4-toluene in methanol or petroleum ether has been heated under reflux for 15 h without alteration in presence of mercuric bromide or 2-butylmercuric bromide. For another, a methanol solution of the substance has reacted in 8 h under reflux without added catalyst to give a 42% yield of bis-4-tolylmercury and a 47% yield of bis-2-butylmercury. Similar anomalies have been found for benzylmercuriethane.

Part of the reason for this lack of reliability has become evident during our attempts to isolate and preserve bis-cyclohexylmercury in a pure state for determination of its dielectric constant (4). The instability of this substance is apparent in its use (5) as a catalyst in the homopolar polymerization of vinyl acetate. We find that the recently crystallized white substance turns grey within an hour in air. If it is vacuum distilled immediately after crystallization, some decomposition occurs during the process, but the distillate is somewhat more stable than the crystalline material before distillation. However, it too begins to turn grey within a few hours. However, if the fresh distillate is

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treated with alkali to decompose any contaminating mercurous salt and then is vacuum distilled, a product is obtained which is quite stable under vacuum or under pure nitrogen so long as it does not contain any peroxide.

It is evident that bis-cyclohexylmercury is very sensitive to oxygen. Indeed, we have been able to measure the dielectric constant in air only after addition of antioxidants. Among those tried the best is 2,5-di-*tert*-butylhydroquinone. Therefore, the oxygen seems to be acting as a source of organic peroxide.

In general, thermal stability of organomercurials (like other organometallic compounds) increases from tertiary to primary with respect to the substituent groups. Therefore, it is not unexpected that bis-benzylmercury, unlike bis-cyclohexylmercury, is stable in air at room temperature.

### $R - Hg - R' \rightleftharpoons R - R' + Hg^{o}$ .

However, bis-benzylmercury without solvent decomposes slowly at  $120-130^{\circ}$  to metallic mercury and 1,2-diphenylethane. In benzene solution this decomposition is much slower but, as may be seen in Table I, it is accelerated by peroxidic catalysts.

TABLE I
Catalyzed decomposition of bis-benzylmercury in benzene (1:2 by weight)

Catalyst				
Name	Mole %	Temp., °C	Time, h	% Hg⁰
None t-Butylperoxide t-Butylhydroperoxide Ascaridole None Mercurous chloride	0 5 5 5 0 5	85–105 Same Same Same 105–110 Same	9 Same Same 3 Same	$  \begin{array}{r}          1 \\          6 \\        $
Acetone peroxide t-Butylperoxide	$\frac{3}{50}$	Same 1 <b>3</b> 0	Same 6	$19 \\ 93^{b}$

<sup>a</sup>41% of 1,2-diphenylethane. <sup>b</sup>69% of 1,2-diphenylethane, of preparative interest.

It would seem that a highly stable peroxide such as ascaridole is especially effective, as might be expected for a slow reaction such as this decomposition. It should be noted that mercurous chloride alone is relatively ineffective.

The catalysis demonstrated according to Table I explains why a comparatively stable unsymmetrical bis-mercurial, 2-butylmercuri-4-toluene, precipitates 55-60% of its mercury content as the metal during 4 h of reflux in the peroxidizable solvent dioxane. Similarly, a boiling methanol solution of the same mercurial to which 0.01% of conc. nitric acid has been added to generate peroxide (6) produces during 6 h *p*-bitolyl, of which 15% precipitates together with 88% of the original mercury in the form of the metal.

We knew that the bis-mercurials mentioned above contained traces of halogen, evidently as the organomercuric halides. Acting on the possibility that the redistribution proceeded via these salts, we have treated benzylmercuric chloride and cyclohexylmercuric chloride under the same conditions and with the same set of peroxidic catalysts as were used with the bis-mercurials. In every instance these salts have been recovered almost unchanged. However, a small amount (2-9%) of mercury and also of mercurous chloride is formed in presence of the peroxides. Thus the organomercuric salts are not catalytically redistributed by peroxides but their decomposition products might be involved.

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With a knowledge of these contaminants in mind, we have now reviewed the redistribution reaction using 2-butylmercuri-4-toluene and benzylmercuriethane as typical disubstituted mercurials. The halogen-containing impurities have been removed from these mercurials by treating them with hydrazine hydrate at room temperature and then distilling them. No redistribution has been detected during distillation.

$$4R-Hg-Cl + 5N_2H_4H_2O \rightarrow 2R-Hg-R + 4N_2H_5Cl + 5H_2O + N_2.$$

The examination of 2-butylmercuri-4-toluene has been made quantitatively with respect to the products, mercury and bis-4-tolylmercury, but only qualitatively with respect to the bis-2-butylmercury because of the tendency for this substance to decompose under some of the reaction conditions. The experiments (with magnetic stirring) have been carried out either in high boiling peroxide-free petroleum ether (S) or else neat (N, without solvent). Temperature, time, catalyst, and supernatant atmosphere (air or nitrogen) have been varied as shown in Table II.

It is evident from expts. 1 and 2 that the uncatalyzed reaction is impracticably slow. Moreover, substances like alkylmercuric halides (expts. 3, 5) are not effective catalysts, with or without peroxides, which themselves (expts. 4, 6, and 7) are of very low activity. In fact, the first substance which shows a significant effect is mercuric chloride (expt. 9), but the enhancement achieved by addition to it of metallic mercury (itself ineffective) shows (expt. 10) that a lower valence state is functioning. Involvement with mercurous chloride is indeed shown by the effectiveness of this substance with or without metallic mercury (expts. 11 and 12).

In fact, the effectiveness of these salts explains some of the erratic behavior characteristic of the redistribution reaction of bis-mercurials. Although Calingaert and his co-workers (3) do not mention any nonhomogeneity of their reacting systems, we have always observed that when redistribution occurs, a dirty second phase is present. Nor from the present findings would the system be expected to be clean. One may expect the following reactions to occur:

$$[2] \qquad \qquad RHgR \xrightarrow{\Delta} RR + Hg$$
peroxide

 $[3] RHgX \rightarrow RX + Hg$ 

$$[4] 2RHgX \rightleftharpoons R_2Hg + HgX_2$$

$$HgX_2 + Hg \rightleftharpoons Hg_2X_2.$$

Reaction [2] has been demonstrated in the present report (reaction [3] has been discovered, though not yet reported) from this laboratory. The equilibrium of reaction [4] will be strongly to the left, if RHgX is present only as a slight contaminant of  $R_2Hg$ . However, this equilibrium is a source of mercuric chloride which enters into the well-known equilibrium of reaction [5]. Thus, a proper combination of these four reactions will furnish some mercurous salt.

Because of a tendency for RHgCl to co-distill and co-crystallize with RHgR, it is very difficult to obtain halogen-free organodisubstituted mercury compounds. We believe that the seemingly spontaneous redistributions reported in the past were due to halogen contamination (and this belief includes our own work before we adopted the purification with hydrazine hydrate). Either because halogen is inadvertently present or else because it is introduced in ostensible catalysts such as Calingaert used, the presence of halogen will give rise to mercurous halide according to reactions [2]–[5]. Therefore, the actual catalyst may, in the past, have been synthesized *in situ*, more or less effectively. If, indeed,

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TABLE 11Redistribution reaction of 2-butylmercuri-4-toluene (1.43 mmole) in 2 ml petroleum ether (S), b.p. 90-100 °C, or without solvent (N)

	-				Desetion		Produc	ts
Expt. No.	Catalyst	Mole %	Gas phase	Solvent	time,	Temp. °C	Bis-p-tolyl- mercury, %	Hg⁰, mg
1	None	0	Air	S	4.5	95	0.2	0
<b>2</b>	None	0	Air	Ν	3.5	95	3.6	1
3	2-Butylmercuric chloride	$^{2}$	Aira	S	4	95	1.0	0
4	<i>tert</i> -Butylperoxide, $(t-bu_2O_2)$	4	Air	S	4.5	95	0.2	0
5	2-Butylmercuric chloride $+ t$ -bu <sub>2</sub> O <sub>2</sub> , 1:1	4	Air	S	4	95	1.0	0
6	Ascaridole	4	Air	S	4.5	95	0.1	1
7	Acetone peroxide	<b>2</b>	Air	S	4.5	95	2.0	1
8	Metallic mercury	<b>2</b>	Air	S	4.5	95	0.2	0
9	Mercuric chloride	<b>2</b>	Air	S	4	95	4.8	1
10	Mercuric chloride plus mercury 1:1	<b>2</b>	Air	S	4	95	9.8	4
11	Mercurous chloride	<b>2</b>	Aira	S	4	95	5.6	6
12	Mercurous chloride plus mercury 1:1	2	Air	S	4	95	11.7	11
13	Mercurous chloride plus $t$ -bu <sub>2</sub> O <sub>2</sub> , 1:1	4	Air	S	4	95	1.8	5
14	Mercurous chloride	$^{2}$	Air	Ν	3.5	95	56.2	18
15	Mercurous chloride	2	Air	N	1.5	95	25.5	
16	Mercurous chloride	$^{2}$	Air	Ν	2.5	90	17.2	
17	Mercurous acetate	$^{2}$	Air	Ν	2.5	90	12.9	
18	Mercurous sulphate	<b>2</b>	$N_2$	S	4	95	66.5	18
19	Mercurous sulphate	<b>2</b>	$N_2$	S	2	80	40.2	9
20	Mercurous sulphate + mercury 1:1	<b>2</b>	$N_2$	S	2	80	68.0	9
21	Mercurous oxalate.H <sub>2</sub> O	<b>2</b>	$N_2$	S	4	95	68.0	6
22	Mercurous oxalate.H <sub>2</sub> O	$^{2}$	$N_2$	S	2	80	24.9	6
23	Mercurous oxalate. $H_2O$ + mercury, 1:1	<b>2</b>	$N_2$	S	$^{2}$	80	31.5	6
24	Mercurous nitrate 2H <sub>2</sub> O	<b>2</b>	Aira	N	2.5	90	68.6	
25	Mercurous nitrate.2H <sub>2</sub> O	<b>2</b>	Air	Ν	1.5	95	74.7	
26	Mercurous nitrate.2H <sub>2</sub> O	$^{2}$	Air	S	4	95	74.1	36
27	Mercurous nitrate.2H <sub>2</sub> O	2	N <sub>2</sub>	S	4	95	69.4	7
28	Mercurous nitrate.2H2O	<b>2</b>	$N_2$	S	$^{2}$	80	49.2	6
<b>29</b>	Mercurous nitrate.2H <sub>2</sub> O	2	N <sub>2</sub>	S	4	40	20.8	6
30	Mercurous nitrate. $2H_{2}O + mercurv$ . 1:1	2	N <sub>2</sub>	S	<b>2</b>	80	42.8	6
31	Mercurous nitrite	2	N,	ŝ	$^{2}$	80	64.3	11
32	Mercurous nitrite + mercury, 1:1	<b>2</b>	$N_2$	S	2	80	59.2	10

<sup>a</sup>The same results were obtained under nitrogen.

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mercurous salt - mercury is the true catalyst, obviously it is better to add it deliberately.

Because of the reversibility of reactions [4]–[5], the effectiveness of additional mercurous salt as a redistribution reaction catalyst is not simply related. Thus, when diethylmercury is heated in acetone with 50 mole % of mercurous chloride, most of the latter is converted to metallic mercury, and ethylmercuric chloride is formed.

# $R_2Hg + Hg_2Cl_2 \rightarrow 2RHgCl + Hg.$

Similarly the reaction of benzylmercuri-2-butane with mercurous chloride yields mercury as well as benzylmercuric chloride and, qualitatively, 2-butylmercuric chloride. However, this heterogeneous reaction [6] is slower in the presence of a nonpolar solvent, or without solvent, than it is in acetone.

The participation of reactions [4]-[5] (i.e. reaction [6]) is quite apparent by the darkening of the surface of a white mercurous salt when it is added to a bis-mercurial either neat or in solvent. But this darkening does not proceed rapidly and only at the end of the reaction period may the mercurous salt largely or completely disappear. That is to say, the presence of mercury seems to retard reaction [4] when it is heterogeneous. This may be simply a mechanical inhibition or, more likely, it may involve a metal-rich intermediate.

# $Hg + X - Hg - Hg - X \rightleftharpoons X - Hg - (Hg)_n - HgX.$

The enhancement of redistribution when metallic mercury is included initially by mortargrinding with mercurous chloride, as shown by expt. 11 vs. 12 and elsewhere in Table II, seems to indicate this involvement. The same effect is observed when twice the amount of catalyst is treated with a half equivalent of hydrazine hydrate.

Among other mercurous salts the acetate (expt. 17) is less effective than mercurous chloride, but the sulphate (expts. 18–20) and the oxalate (expts. 21–23) are more active catalysts. The effect of either is enhanced by inclusion of metallic mercury.

The most effective catalyst is mercurous nitrate (expts. 24–30), but the rate is unaltered by inclusion of metallic mercury. Although mercurous nitrite is less effective than the nitrate, its effectiveness also is unaltered appreciably by added mercury metal which enhances the effect of the chloride, sulphate, and oxalate. This apparent contradiction is resolved by the observation that the nitrite and nitrate generate metal according to reaction [6] from the solution of bis-mercurial much more rapidly than does the chloride, sulphate, or oxalate. Thus sufficient mercury to satisfy eq. [7] is soon present and added metal is superfluous. The ready evolution of the metal may be due to the peroxide-forming tendency of nitrate (and nitrite) salts.

The catalysts that are mentioned in Table II are nominally heterogeneous. There is visual evidence of reaction at the catalyst surface in an unstirred system in which bis-4-tolylmercury or bis-benzylmercury appears as a crystalline solid because the crystals seem to be growing from the mass of darkened mercurous salt. Of course the catalysis might actually be homogeneous despite this appearance. We have found difficulty in making a firm decision because systems which are strictly homogeneous cause reaction alternative to redistribution. The inclusion of acid to bring about homogeneity causes demetalation.

Since mercurous nitrate is somewhat soluble in methanol, a solution has been refluxed containing 1 equivalent of 2-butylmercuri-4-toluene, 0.02 equivalent of mercurous nitrate, and a small amount of nitric acid sufficient to make a clear solution. After 6 h, 0.9 equivalent of the mercury precipitated as the metal and no bis-4-tolylmercury was isolable. Instead p-bitolyl was found. Elimination of the nitric acid from the system reduces metal formation markedly and a 19% yield of the symmetrical bis-4-tolylmercury was obtained, but the system was cloudy (heterogeneous) in absence of the nitric acid. A relatively

[6]

[7]

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clearer solution is obtained without acid when the 2-butylmercuri-4-toluene and 0.02 equivalent of mercurous nitrate are refluxed 4 h in peroxide-free dioxane under nitrogen, but redistribution, as exemplified by bis-4-tolylmercury, occurs only by a few percent despite precipitation of about 0.02 equivalent of metallic mercury. In summation, the catalysis does not seem to be homogeneous but our proof is equivocal.

Likewise, it might be doubted whether our redistribution catalyst is alternative to those reported by Calingaert *et al.* or whether the substances that they used for catalysis actually generated mercury plus mercurous salt. They do not describe their reaction systems in sufficient detail to disclose whether a nondescript second phase is present. We have attempted to simulate their systems by comparing the effectiveness of mercurous chloride plus mercury on the one hand with aluminium chloride, and on the other at room temperature with four bis-mercurial combinations: benzylmercuriethane, bis-ethylmercury plus bis-*p*-tolylmercury, 2-butylmercuri-4-toluene and bis-2-butylmercury plus bis-4-tolylmercury. With either of the two catalysts the systems did not come to equilibrium even after 140 h, but they are about equally effective. Moreover, the two catalysts resemble each other in appearance while the reactions are proceeding. It is our opinion that aluminium chloride is effective as a catalyst for redistribution because it reacts with bismercurials that are present to give mercurous chloride and mercury.

The evidence for this opinion is the presence of metallic mercury among the final products. Although mercurous chloride could not be identified, its presence may be expected during the reaction if the following equations are valid.

[8] 
$$R_2Hg + AlX_3 \leftrightarrows RHgX + RAlX_2$$

$$[9] RHgX + AlX_3 \leftrightarrows RHg^+(AlX_4)^-$$

 $[10] \qquad \qquad RHg^+ \rightarrow R^+ + Hg^0$ 

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Equation [8] is well known; indeed Calingaert invoked it (1) in his mechanism according to which he would consider RHgX to be the catalyst. Since the present study excludes this type as the direct catalyst, we suggest that metallic mercury is formed according to [9]–[11] because the RHg<sup>+</sup> cation will be unstable (7). Since mercuric halide is potentially available from the equilibrium [4], the initial presence of mercurous halide may be expected in view of [5]. Therefore the catalyst combination, mercurous salt plus mercury, can arise from aluminium chloride and bis-mercurial.

Of course, a reaction which is accelerated by a material catalyst should proceed satisfactorily without that catalyst, if the temperature is sufficiently raised, providing of course that the system (or part of it) is otherwise stable. Rausch has reported (8) that methylmercuribenzene, as well as bis-methylmercury plus bis-phenylmercury, undergoes the redistribution reaction cleanly and to almost the same equilibrium. Evidently, no metallic mercury is formed. This is a necessary condition since if one of the three bismercurials in the system were thermally more or less stable than the others a false equilibrium value might be observed, depending on the relative rates of the redistribution versus the demetalation reaction. The error would not necessarily be detected by the alternative directions of approach to equilibrium. Since Rausch did not report any metallic mercury in his redistribution reaction, it would seem that bis-methylmercury, bisphenylmercury, and methylmercuribenzene all are equally stable at 150°. But this circumstance may not prevail with other substituent groups.

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The error would easily be detectable if R-Hg-R or R'-Hg-R' were much less stable than R-Hg-R', especially if the redistribution rate were slow, i.e., if  $k_4$  or  $k_5 \gg k_2 > k_3$ ,



This circumstance is apparent in the following two examples. When 2-butylmercuri-4toluene on the one hand, and an equimolar mixture of bis-2-butylmercury and bis-4tolylmercury on the other, are heated at 140–150° under nitrogen for 4.5 h the amounts of mercury precipitated are 7% and 30% respectively. The system initially containing the mixed bis-mercurial yields 45% of the bis-4-tolylmercury expected if the distribution were random, while the system initially two-component yields 167% of the bis-4-tolylmercury expected upon random distribution. Clearly, in this case, the bis-2-butylmercury has demetalated at a rate faster than redistribution equilibrium can be established.

An extreme case where redistribution is impossible at high temperatures is shown by an initially equivalent mixture of bis-ethylmercury and bis-benzylmercury. When this mixture is heated to  $140-150^{\circ}$  for 4.5 h, 50% of the total mercury is precipitated as the metal. Except for traces, all that is left is bis-ethylmercury, the dibenzylmercury having been demetalated completely.

From these results it is apparent that thermal redistribution equilibration is impractical when secondary alkyl, aralkyl, and other electropositive substituents are involved.

It is apparent that if one disregards the obvious basis of error, i.e. appearance of metallic mercury, a false value for equilibrium will be obtained if  $k_3 > \text{or} = k_2 > k_4 = k_5$  because the equal amounts of bis-mercurials in the product will be misleading. Perhaps it is fortuitous that unsymmetrically disubstituted mercury is frequently more stable thermally than the bis-mercurials to which redistribution would convert it, so that this error will be unlikely. However, one cannot be certain that this rule is unequivocal and circumstances where  $k_1-k_5$  are all of the same order of magnitude may exist and lead to erroneous conclusions. When secondary or tertiary alkyl, aralkyl, or other electropositive substituents are present, the precipitated metal may be expected during high-temperature redistribution. In this circumstance an equilibrium value is unreliable.

At lower temperatures in hydrocarbon solvent one may with some bis-mercurials get a meaningful value for equilibrium by use of catalyst such as mercurous nitrate. Table III shows how the value is chosen for the benzyl-ethyl-mercury system. Comparison of uncatalyzed expts. 1 and 5 of Table III shows that neither represents a state of equilibrium, but it does indicate that  $k_2$  is larger than  $k_1$ . These magnitudes are reflected in the approximate constant  $k_1/k_2$  of about 0.24 which may be derived from the data of expts. 2 and 3 where the region of equilibrium seems to be established. The value should be accepted with some reservation in view of the amount of metallic mercury which is evolved. However, it may be noted that expt. 4 at room temperature produces about the same amount of metal, although equilibrium seems not to have been attained. It would seem from expt. 4 that the production of metal is not due to a high-temperature demetalation.

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## TABLE III

Redistribution with stirring in 2 ml of petroleum ether (b.p. 90-100°) per mmole of  $R_2Hg$  where R = ethyl or benzyl, using 4 mole % of mercurous nitrate dihydrate as catalyst

Evet	Disubs	Disubstituted mercury, mmole		Catalant		т	TT- 0	Final	
No.	Diethyl	Dibenzyl	Ethyl benzyl	mole	h	°C	mg	R₂Hg, mmoles	
I Initial Final	1.00 0.80	$\begin{array}{c}1.00\\0.82\end{array}$	0.30	0	24	90-92	2	1.92	
2 Initial Final	$\begin{array}{c}1.00\\0.74\end{array}$	$\begin{array}{c}1.00\\0.77\end{array}$	0.40	4	24	90-92	19	1.91	
3 Initial Final	0.74	0.78	$\begin{array}{c} 2.00\\ 0.33 \end{array}$	4	24	90-92	20	1.85	
1 Initial Final	0.62	0.58	$\begin{array}{c} 2.00\\ 0.46\end{array}$	$2+2^{a}$	385	25	17	1.66	
5 Initial Final	0.33	0.33	2.00 1.22	0	24	90-92	1	1.88	

<sup>a</sup>After 80 h the initial 2 mole % of catalyst was augmented by 2 mole % more.

## TABLE IV

Redistribution under nitrogen in petroleum ether (b.p.  $90-100^{\circ}$ ) of R<sub>2</sub>Hg where R = 2-butyl and 4-tolyl using mercurous nitrate dihydrate as catalyst

		Disubstit	uted mercur	y, nımole		C 1 (			
	Expt. No.	Di-2-butyl	Ditolyl	2-Butyl 4-Tolyl	Catalyst, mole %	ml per mmole	Temp., °C	Hg⁰, mg	Time, h
1	Initial Final	0.08	0.09	2.00 1.68	0	1	86-88	0	6
2	Initial Final	$\begin{array}{c}1.00\\0.67\end{array}$	$\begin{array}{c} 1.00\\ 0.96 \end{array}$	0.04	0	3	89-91	35	108
3	Initial Final	0.48	0.67	$\begin{array}{c} 2.00 \\ 0.50 \end{array}$	2	0.75	80-85	6	8
4	Initial Final	0.48	0.63	$\begin{array}{c} 2.00\\ 0.68 \end{array}$	4	1	86-88	7	6
5	Initial Final	0.76	0.83	2.00ª 0.32	4	1.7	90-92	12	24
6	Initial Final	0.63	0.64	$\begin{array}{c} 2.00\\ 0.70\end{array}$	4	1.7	25	5	330
7	Initial Final	$\begin{array}{c} 1.00\\ 0.65 \end{array}$	1.00 0.96	0.07	2	1.2	80-85	17	8

<sup>a</sup>Magnetically stirred.

Attempts to find the redistribution equilibrium for the system bis-2-butylmercury plus bis-4-tolylmercury  $\rightleftharpoons 2$ -butylmercuri-4-toluene have not been so satisfactory according to Table IV. Evidently the difficulty is due to the instability of bis-2-butylmercury as may be seen by comparison of expts. 1 and 2 where a catalyst is not involved and of expts. 2 and 7 where bis-2-butylmercury is present initially. The same disparity between the unstable secondary bis-mercurial and the aromatic bis-mercurial is seen in expts. 3–4. As may be seen in expt. 6 the instability problem may be compensated by low temperature and long duration, but it is doubtful whether equilibrium has been reached. Actually expt. 5 in which the system is stirred gives values which may be close to equilibrium, in which case  $k_1/k_2$  is about 0.17. Whether or not expts. 6 and 5 approach or reach equilibrium, the direction is such that the equilibrium constant cannot equal four.

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If the redistribution reaction of organodisubstituted mercury were a random exchange process regardless of the polarity of the substituents as Calingaert *et al.* have tried to demonstrate, then the equilibrium constant ought to be four. As may be seen from the results of Tables IV and V, the observed equilibria, even if they are in error, could never conform to the Calingaert condition. We suggest that the small difference in polarity among the lower alkyl groups that form the basis for Calingaert's postulation are not sufficiently different in polarity to warrant a generalization about the redistribution reaction. If the term "redistribution" has become associated with randomization then this association ought to be discontinued.

TABLE V								
Attempted	equilibration	bу	means	of	aluminium	chloride	2	

Expt. No.	Disul	Time, h	Hg⁰, mg		
1 Initial Final	Bis-2-butyl 3.92 2.96	Bis-4-tolyl 3.92 3.36	2-Butyl, 4-tolyl None 0.53	137	30
2 Initial Final	Bis-2-butyl None 0.14	Bis-4-tolyl None 0.23	2-Butyl, 4-tolyl 4.33 3.58	139	50
3 Initial Final	Bis-ethyl 3.92 2.08	Bis-benzyl 3.92 3.30	Ethyl, benzyl None 0.73	141	110
4 Initial Final	Bis-ethyl None 0.21	Bis-benzyl None 0,26	Ethyl, benzyl 3.90 2.56	117	45

It follows also that if randomization is not characteristic of the redistribution reaction then the correlative concept that redistribution occurs via free radical transfer likewise has no experimental basis.

## EXPERIMENTAL\*

## Bis-cyclohexylmercury, Halogen and Peroxide Free

The stirred Grignard reagent prepared in 85% yield, 0.34 mole, from cyclohexyl bromide (9), b.p. 88° (76 mm),  $n_{\rm D}^{14}$  1.49572, m.p. -49 to -48, was treated slowly under nitrogen with 50.4 g (0.14 mole) of dry mercuric bromide during 9 h at 25° and then was poured onto crushed ice. After acidification of the system with 30 ml of acetic acid the nonaqueous layer, dried with magnesium sulphate, was evaporated, leaving 44 g (86%) melting above 70°. This crude product in 15 ml of diethyl ether was treated with 10 ml of 99-100% hydrazine hydrate in the dark during a minimum time of 20 h. After addition of 10 ml of water and separation of the aqueous phase the latter was twice extracted with ether which was added to the nonaqueous phase. The combined ether solution, washed once with water, was dried with magnesium sulphate, and distilled at 125° (1 mm). The distillate, m.p. 76-78°, which contained some mercury, was crystallized from absolute ethanol, m.p. 78-79°. This product will begin to decompose in air after several hours, but will remain white for long periods under nitrogen or in vacuum. It may be stabilized for 24 h in air, if it is dissolved in acetone containing 2% of 2,5-di-*tert*-butylhydroquinone and the resulting solution evaporated to dryness *in vacuo*. A portion heated to 170 °C *in vacuo* (2.43 mmole) liberated cyclohexene according to infrared absorption at 3.32 and 5.92  $\mu$ . The thermal stability of this bis-mercurial at 25° was not decreased by contamination with mercurous chloride.

#### Benzylmercuriethane, Halogen and Peroxide Free

The Grignard reagent from 0.09 g-atom of magnesium and 0.09 mole of ethyl bromide in 150 ml of diethyl ether was stirred under nitrogen at +4 °C while 11.7 g (35.8 mole) of benzylmercuric chloride, m.p. 105.5-106°, (10) was added in small portions during 15 min. After 30 min subsequent stirring the system was poured into a mixture of ice plus 1% aqueous sulphuric acid. The aqueous layer was twice extracted with peroxide-free diethyl ether and the entire nonaqueous portion, dried with magnesium sulphate, was distilled finally at 0.04 mm to give 10.9 g (70%) of benzylmercuriethane, b.p. 89–91°. The distillation residue yielded 0.6 g of bis-benzylmercury, m.p. 108–110.

\*Melting points have been corrected against reliable standards.

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# FRENCH ET AL.: REDISTRIBUTION OF BIS-MERCURIALS

The crude product in 10 ml of diethyl ether was treated with 10 ml of 95–100% hydrazine hydrate. After the mixture was stirred for at least 24 h, 10 ml of water was added and the aqueous layer was extracted with peroxide-free ether. The combined ether solution, twice washed with water and dried with magnesium sulphate, was distilled at 0.01 mm, b.p. 85–90 °C, in 78% recovery.

## 2-Butylmercuri-4-toluene, Halogen and Peroxide Free

The Grignard reagent, from 0.156 g-atom of magnesium and 0.155 mole of *p*-bromotoluene, in 270 ml of diethyl ether was stirred at -11 °C while a solution of 31.15 g (0.092 mole) of 2-butylmercuric bromide (11), m.p. 42.5-43 °C, in 260 ml of diethyl ether was added during 35 min. After 30 min stirring at the same temperature the whole was poured into a mixture of ice and 1% aqueous sulphuric acid. The aqueous layer was extracted with peroxide-free ether. The combination of nonaqueous parts was washed with water and then was stirred with 20 ml of 99-100% hydrazine hydrate for 24 h. The nonaqueous layer was separated, dried with magnesium sulphate, and distilled finally at 95-100° (0.01 mm) to yield 30.1 g (94%).

When (+)2-butylmercuric bromide,  $[\alpha]_D^{28} = +3.24^\circ$  in acetone, was used in this preparation the resulting 2-butylmercuri-4-toluene gave 2-butylmercuric bromide, m.p.  $34-35^\circ$ ,  $[\alpha]_D^{28} = +2.80^\circ$  in acetone, when it was treated with 1 equivalent of mercuric bromide in methanol.

#### Benzylmercuric Chloride with Peroxides

A solution of benzylmercuric chloride (0.5 g) in benzene containing 4.3 mole % of ascaridole, *tert*-butyl hydroperoxide, or di-*tert*-butyl peroxide in 2 ml of benzene was heated to 110° for 3.5 h. The rest was taken up in benzene to leave 10–15 mg of mercurous chloride (black with alkal, positive for chlorine upon elemental analyses). The benzene solution upon evaporation left 410 mg (82%) unchanged chloromercurial, m.p. 105.5–106°.

### Preparation of Mercurous Salts

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Mercurous oxalate monohydrate was prepared in 99% yield by treating (12) a solution of 1.12 g of mercurous nitrate dihydrate in 3 ml of water containing 10 mg of conc. nitric acid with 0.5 g of oxalic acid with shaking. The precipitate was filtered, washed with water, acetone, and ether, and dried *in vacuo*. The salt did not lose water at  $60^{\circ}$  *in vacuo* for 22 h.

Mercurous sulphate was prepared in 33% yield (13) by treatment of 1.12 g of mercurous nitrate dihydrate in 3 ml of water plus 10 mg of conc. nitric acid with 2 ml of 30% aqueous sulphuric acid. The precipitate was washed with water and vacuum dried.

Mercurous nitrite was prepared by treating a solution of 5 ml conc. nitric acid and 15 ml of water with 20 g of metallic mercury at 30–35° for 5 h and then at 25° for 3 days. The filtrate from this sytem when cooled gave white crystals instead of yellow ones (14). They gave a positive Liebermann test. According to the mercurous chloride obtained from 300 mg, this salt is the dihydrate of the monomeric species.

#### Redistribution with Aluminium Chloride

The experiments summarized in Table V were effected in petroleum ether (b.p. 40-60, 3 ml for the unsymmetrical and 6 ml for the symmetrical mercurials) at 20-25° and were processed after reaction by filtration; the filtrate was treated with water, then dried and distilled. The initial precipitate was extracted with benzene, leaving dirty metallic mercury. Evaporation of the benzene left the petroleum ether insoluble bis-mercurial.

#### Preparation of Mercurous Salt - Mercury Metal Systems

Generally the ingredients were ground in a mortar until the metal was no longer visible. In one instance 1.12 g of mercurous nitrate was suspended in 1 ml of water to which 39 mg of 100% hydrazine hydrate was added. The suspension was filtered after 10 min and washed with water and acetone, then vacuum dried.

### Bis-ethylmercury with Mercurous Chloride

A system comprised of 1.61 g (3.42 mmole) of mercurous chloride and 1.77 g (6.84 mmole) of bis-ethylmercury in 30 ml of acetone was heated for 1 h. The mercurous chloride gradually was converted to metallic mercury. After 15 h the metal was filtered off, 0.675 g (97%). The filtrate was evaporated and the residue (1.95 g) was washed with petroleum ether, b.p. 40–60°, leaving 0.80 g (88%) of ethylmercuric chloride, m.p. 190–192°.

#### Redistribution Reaction, Heterogeneous Catalyst

Reactions were carried out in 25 ml Erlenmeyer flasks under a reflux condenser in a temperature-regulated bath. When stirring was desired a glass-covered Kovar bar was used with magnet drive. Some reactions were carried out under air and some under nitrogen. When petroleum ether (b.p. 90-100°) was used it was dry, free from unsaturated impurities, and peroxide free.

Upon completion, the insoluble part was filtered off and washed with petroleum ether (b.p. 40-60°), dried, and weighed. Then it was extracted with benzene if bis-4-tolylmercury was to be removed or with acetone if it contained bis-benzylmercury. The spent catalyst (principally metal) was then weighed to obtain by difference the yield of bis-benzylmercury or bis-4-tolylmercury. The extracts were vacuum evaporated at room temperature via a dry ice cooled trap, and the weighed residue was distilled. The boiling points of the

several products are: bis-ethylmercury, b.p. 72-74° (35 mm); bis-2-butylmercury, 45-48° (0.8 mm); benzylmercuriethane, b.p. 85-88° (0.01 mm); benzylmercuri-2-butane, b.p. 90-94° (0.02 mm); 2-butylmercuri-4toluene, b.p. 105-110° (0.06 mm). Since the first two of these products tended to co-distill with the solvent the cold-trap content was treated with an amount of mercuric bromide in acetone, which was equivalent to the difference between the theoretical yield and the amount obtained by distillation. After 1 h this system was vacuum evaporated. From the increased weight the additional dialkylmercury could be calculated. The distilled dialkylmercury was also dissolved in acetone or methanol and treated with an equivalent amount of mercuric bromide, to identify the distillate by the melting point of the corresponding alkylmercuric bromide.

The residues in the flasks after distillation were dissolved in benzene or acetone, filtered, vacuum evaporated, washed with petroleum ether, b.p. 40-60, and dried before weighing as bis-4-tolylmercury (m.p. 243-245°) or bis-benzylmercury (m.p. 110-111°).

# Redistribution Reaction, "Homogeneous Catalyst"

A cloudy system of 0.5 g (1.43 mmole) of 2-butylmercuri-4-toluene and 16 mg (0.029 mmole) of mercurous nitrate in 15 ml each of water and methanol plus 25 ml of acetone was heated for 6 h under reflux at a bath temperature of 83-90°. Subsequently 70 ml of water was added and the remaining precipitate was filtered off, weight 220 mg containing mercury. Extraction with benzene left 150 mg, largely mercury. Evaporation of the benzene solution left 70 mg (19%) of bis-4-tolylmercury, m.p. 241-243°. Similar results were obtained when the reaction medium was methanol alone, but the yield, m.p. 240-242°, was only 5 mg when dioxane was the medium.

When 5 mg of conc. nitric acid was included in the system where methanol alone was used, the precipitation of metal was very large (250 mg) and the isolable product was 4,4'-ditolyl, m.p. 115-118°. These products were the same in type and yield when mercurous nitrate was not included in the system.

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