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Redistribution Equilibria of Some Organomercury Compounds[1]

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By means of gas chromatography and nuclear magnetic resonance, equilibrium constants were obtained for the exchange of organic groups in the systems diethylmercury–dimethylmercury, diethylmercury–di-*n*-propylmercury, diethylmercury–diisopropylmercury, diethylmercury–dicyclopropylmercury, diethylmercury–divinylmercury, diethylmercury–diphenylmercury, divinylmercury–diphenylmercury, divinylmercury–dicyclopropylmercury, bis(perfluoroisopropyl)mercury–diisopropylmercury, and bis(perfluoroisopropyl)mercury–di-*n*-propylmercury. The results show that the redistribution equilibria are dependent upon the nature of the exchanging groups and may deviate widely from randomness.

Introduction

In order to determine the effect of varying the organic groups (R and R′) on the redistribution equilibria

$$R_2Hg + R'_2Hg \rightleftharpoons 2RR'Hg$$

the equilibrium concentrations of the three possible species were determined for various binary mixtures of organomercury compounds. Although proceeding only very slowly at room temperature, the uncatalyzed redistributions were found to proceed to equilibrium upon heating to 90° over the period of several days. The degree to which the various equilibria deviated from that of a purely statistical redistribution could be determined by comparing the calculated equilibrium constants with the expected value of $K_{eq} = 4$ for the random exchange, where

$$K_{eq} = (\text{mole fraction of } RR'Hg)^2/(\text{mole fraction of } R_2Hg)(\text{mole fraction of } R'_2Hg)$$

The reaction mixtures were analyzed by gas chromatography except for those mixtures containing diphenylmercury, which were analyzed by nuclear magnetic resonance due to the insufficient volatility of the diphenylmercury.

Only a few redistribution reactions of organomercury compounds have been reported in the literature. In his original work on the redistribution reaction, Calingaert[4] reported that an equimolar mixture of dimethylmercury and diethylmercury redistributed after 18 hr in the presence of aluminum trichloride catalyst to give an essentially random mixture of products. More recently, equilibrium constants have been measured for the systems dimethylmercury–diphenylmercury ($K_{eq} = 4.4$, or random within experimental error) and dimethylmercury–bis(perfluorophenyl)mercury,[5] in which K_{eq} is greater than 2×10^3, giving essentially complete conversion to the unsymmetrical product.

Experimental Section

Materials.—Dimethylmercury, diethylmercury, and diphenylmercury were purchased from the Eastman Kodak Co., divinylmercury was purchased from Orgmet Co., and di-*n*-propylmercury and diisopropylmercury were purchased from K & K Laboratories. Bis(perfluoroisopropyl)mercury and bis(perfluoro-*t*-butyl)mercury were a gift from the E. I. du Pont de Nemours and Co. Dicyclopropylmercury was prepared as previously described.[6]

Cyclopropylethylmercury was prepared by the reaction of cyclopropylmagnesium bromide and ethylmercuric chloride in tetrahydrofuran in a manner analogous to that of Hilpert and Gruttner[7] for the preparation of unsymmetrical organomercuries.

Ethylphenylmercury was also prepared by the Hilpert and Gruttner method using tetrahydrofuran as the solvent.

All of the organomercury compounds were stored in brown bottles at 0°. Before each use of these compounds in redistribution experiments, the purity of each was checked by gas chromatography, and, when necessary, they were purified by vacuum distillation. The two exceptions were the solid compounds diphenylmercury and bis(perfluoro-*t*-butyl)mercury. Since these two compounds showed no tendency to decompose, they were used without further purification.

Analytical Techniques.—The gas chromatographic analyses were performed with a Perkin-Elmer Model 154 vapor fractometer equipped with a 2-m DC-200 silicon (2.5% by weight on chromosorb W, 80–100 mesh) column. The area under each peak of the chromatogram was taken as proportional to the concentration of the species responsible for the peak. Peak areas were determined by cutting out and weighing the paper under the peak trace, the weight ratios being used for the relative mole ratios of the different species. Calibration of this technique with known concentrations of symmetrical organomercury compounds indicated a reproducibility to within 1%. In those few cases where two of the three peaks were not completely resolved, the combined peak area was apportioned to the two species involved from consideration of the initial molar ratio of the mixture and from the stoichiometry of the reaction.

The nuclear magnetic resonance analyses were performed with a Varian A-60 spectrometer. This method of analysis was used for the systems containing diphenylmercury; quantitative information was obtained from the sharp resonances due to the phenyl protons. The areas under the various phenyl peaks were determined by means of the integrator, the identity of the peaks being determined by comparison with pure diphenylmercury. In each case, the peak areas were normalized by dividing by the number of phenyl groups per molecule. With this correction, the area ratios were set equal to molar ratios. The relative concentration of the third component was then determined by difference. Preliminary trials with a mixture containing known amounts of

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(4) G. Calingaert, H. Soroos, and V. Hnizda, *J. Am. Chem. Soc.*, **62**, 1107 (1940).

(5) M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964).

(6) G. F. Reynolds, R. E. Dessy, and H. H. Jaffé, *J. Org. Chem.*, **23**, 1217 (1958).

(7) S. Hilpert and G. Gruttner, *Ber.*, **48**, 906 (1915).

diphenylmercury and diethylmercury indicated that the quantitative accuracy to be expected was approximately ±3%.

Redistribution Reactions.—With the exception of the redistribution reactions involving the perfluoroalkylmercury compounds, the reactions were run without solvent or catalyst. The appropriate quantities (0.05–0.50 g) of the organomercuries were weighed into small vials which had been flushed with dry nitrogen. The weights were recorded and used to calculate the initial mole fractions of the two reactants. Aliquots (20 μl) of this mixture were then transferred to 1-ml glass vials which had been flushed with nitrogen. These vials were cooled under nitrogen in a Dry Ice–acetone bath and sealed. This procedure was repeated until five or six sets of samples of different initial molar ratios were prepared. The vials were completely submerged in an oil bath at 90 ± 2°. One vial of each set was removed from the bath every 24 hr and analyzed. This procedure was repeated until two subsequent analyses yielded the same relative concentration of the three species within experimental error. At least one vial was left in the bath for a longer time (about 200 hr) to provide a further check on the attainment of equilibrium. As an additional test of equilibrium, reverse reactions were run using the newly prepared unsymmetrical organomercuries—ethylcyclopropylmercury and ethylphenylmercury.

In the case of the bis(perfluoroisopropyl)mercury–diisopropylmercury and bis(perfluoroisopropyl)mercury–di-*n*-propylmercury systems, the immiscibility of these mixtures necessitated the use of a solvent. The same procedure was followed with the modification that 0.5 ml of toluene was added to each sample to provide homogeneity. That this modification appeared to have no effect on the redistribution equilibria was verified by repeating the reaction of the dimethylmercury–diethylmercury system in toluene solution. Toluene was also used as a solvent in redistributions involving bis(perfluoro-*t*-butyl)mercury; however, the results were questionable since some immiscibility was noted when the samples were cooled for gas chromatographic analysis.

Results

The wide variation in boiling points of the compounds which were analyzed by gas chromatography required different experimental conditions with the type of column employed. Preliminary trials were undertaken to find the conditions for each system which yielded the best chromatographic analysis for that system. These conditions are recorded in Table I, along with the retention times which are given to the nearest minute. The retention times are characteristic of the components of the organomercury mixtures and were used as a basis for species identification.

The experimental results for the different systems studied by gas chromatography and nuclear magnetic resonance are given in Table II. In cases where the redistribution reaction proceeded far to the right, measurements for mixtures in which one component was very much in excess proved inaccurate and therefore are not included in the tabulation. Because quenching and analysis times were short compared to the total reaction time necessary to reach equilibrium, the equilibrium data given here are approximately that for the mixture at 90° at which the redistributions were carried out. It is interesting to note that the same equilibrium constant was obtained using a mixture of pure diethylmercury–dimethylmercury as was obtained when toluene was added as a solvent. The only difference noted was a longer reaction time necessary to reach equilibrium when the solvent was used.

TABLE I

CONDITIONS EMPLOYED FOR GAS CHROMATOGRAPHIC ANALYSES

System components	Retention time, min	Temp, °C	Flow rate, ml/min
$(CH_3)_2Hg$	2	75	250
$C_2H_5HgCH_3$	4		
$(C_2H_5)_2Hg$	9		
$(C_2H_5)_2Hg$	2	110	450
c-$C_3H_5HgC_2H_5$	6		
$(c$-$C_3H_5)_2Hg$	16		
$(C_2H_3)_2Hg$	2	80	300
$C_2H_3HgC_2H_5$	6		
$(C_2H_5)_2Hg$	7		
$(C_2H_3)_2Hg$	1	110	450
$(c$-$C_3H_5)_2Hg$	16		
$(C_2H_5)_2Hg$	4	60	600
n-$C_3H_7HgC_2H_5$	8		
$(n$-$C_3H_7)_2Hg$	13		
$(C_2H_5)_2Hg$	4	60	600
i-$C_3H_7HgC_2H_5$	8		
$(i$-$C_3H_7)_2Hg$	15		
$(i$-$C_3F_7)_2Hg$	1	70	500
n-$C_3H_7Hg(i$-$C_3F_7)$	2		
$(n$-$C_3H_7)_2Hg$	8		
$(i$-$C_3F_7)_2Hg$	1	70	500
i-$C_3H_7Hg(i$-$C_3F_7)$	2		
$(i$-$C_3H_7)_2Hg$	9		

The results for the redistributions of the bis(perfluoro-*t*-butyl)mercury–di-*n*-propylmercury and the bis(perfluoro-*t*-butyl)mercury–diisopropylmercury systems carried out in toluene are not included in the tabulation of Table II since some immiscibility was noted in the samples which were quenched for analysis. However, the equilibrium constants for these two systems appeared to be quite large.

Discussion

Contrary to the earlier work which predicted random exchange for the redistribution of organomercury compounds,[4] the results of this study indicate that the purely statistical exchange may be the exceptional case, occurring only when the two organic groups are almost identical in nature. The redistribution of ethyl and *n*-propyl groups on mercury at 90° results in an equilibrium constant of 4.5 which is close to the expected value of $K_{eq} = 4$ for the random exchange. However, for the exchange of ethyl and methyl groups under the same conditions, the equilibrium constant is less than half that expected for random exchange, indicating that in this case the symmetrical species are preferred in the redistribution reaction.

Comparison of the result for the diethylmercury–diisopropylmercury exchange with that for the diethylmercury–di-*n*-propylmercury exchange shows a slightly larger equilibrium constant for the former case. This suggests that a steric factor is responsible for the unsymmetrical product being more favored in the exchange of ethyl and isopropyl groups. However, the magnitude of any steric effect appears too small to account for the large deviations from randomness found for the exchange of other groups reported in this work.

TABLE II

EQUILIBRIUM RESULTS FOR THE REDISTRIBUTIONS $R_2Hg + R'_2Hg = 2RR'Hg$ at 90°

R–R′	Initial molar R:R′ ratio	Mole % of total mercury			K_{eq} (av)	Std dev
		R_2Hg	$RHgR'$	$R_2'Hg$		
CH_3–C_2H_5	0.53	12.9	34.6	52.5	1.8	0.26
	0.74[a]	24.5	39.1	36.5		
	0.93	28.9	40.5	30.6		
	1.00	29.5	40.8	29.7		
	1.92	53.4	31.8	14.8		
C_2H_5–*c*-C_3H_5	0.75	6.0	83.5	10.5	130	16
	1.00	7.4	86.0	6.6		
	1.00[b]	7.1	85.8	7.1		
	1.30	11.1	84.0	4.9		
	1.55	18.2	79.1	2.7		
C_2H_5–C_2H_3	0.44	1.1	59.2	39.7	86	10
	1.19	14.0	81.2	4.8		
	3.22	53.1	46.4	0.5		
C_2H_5–C_6H_5	1.00[b]	23.4	53.2	23.4	5.0	0.14
	1.26	29.7	52.2	18.1		
	1.71	38.7	48.8	12.5		
	3.88	62.6	33.8	3.6		
C_2H_3–C_6H_5	0.41	3.6	51.0	45.4	15	0.71
	0.60	7.4	60.2	32.4		
	1.63	31.8	60.4	7.8		
	3.65	58.6	39.7	1.7		
C_2H_3–*c*-C_3H_5	. . .[c]					
C_2H_5–*n*-C_3H_7	0.19	2.3	27.0	70.7	4.5	0.17
	0.42	8.4	42.2	49.4		
	1.03	24.9	51.6	23.5		
	2.86	54.3	39.6	6.1		
C_2H_5–*i*-C_3H_7	0.41	7.2	43.6	49.2	5.3	0.15
	1.50	34.3	51.4	14.3		
	3.24	57.6	37.6	4.8		
	7.85	78.4	20.6	1.0		
n-C_3H_7–*i*-C_3F_7[a]	0.66	0.1	79.6	20.3	$>2 \times 10^3$	
	0.93	0.3	95.8	3.9		
i-C_3H_7–C_3F_7[a]	0.60	0.1	74.8	25.1	$>2 \times 10^3$	
	0.96	0.7	96.4	2.9		
	1.10	4.9	94.8	0.3		

[a] These samples reacted in toluene solution. [b] These samples were the newly prepared unsymmetrical organomercuries. [c] Under the conditions employed in this study, no evidence of redistribution could be found in this system after 2 weeks.

The equilibrium constants for the organomercury redistributions where one of the components is fluorinated are very large, forming almost exclusively the mixed product, in agreement with previous results for the bis(perfluorophenyl)mercury system.[5] The exchanging ligands in the case of the diisopropylmercury–bis(perfluoroisopropyl)mercury and di-*n*-propylmercury–bis(perfluoroisopropyl)mercury redistributions differ principally in the high electronegativity of the perfluoroalkyl groups. Fluorination causes the central mercury atom of the bis(perfluoro)mercuries to become more electron accepting and susceptible to reaction with electron-donating groups. Evidence of this comes from a study of bis(perfluorophenyl)mercury[8] which was found to form stable coordination compounds with suitable donor molecules.

The results obtained in the diethylmercury–divinylmercury, diethylmercury–dicyclopropylmercury, and diethylmercury–diphenylmercury redistributions may also be attributable to the greater electron-accepting ability of the mercury atom attached to the vinyl, cyclopropyl, and phenyl groups owing to the unsaturation of these groups. There are of course steric factors to consider in these cases also, but the magnitude of the steric effect cannot account for the results observed, which for the vinyl and cyclopropyl cases show that the unsymmetrical species is very much preferred. The value of K_{eq} for the diethylmercury–diphenylmercury exchange seems to be unexpectedly small by comparison. A possible explanation for this may be the resonance interaction between phenyl groups of the diphenylmercury which is lost upon the formation of the unsymmetrical product. It is interesting to note that in the case of the diphenylmercury–divinylmercury exchange, where resonance interaction can still occur in the unsymmetrical species, the equilibrium constant indicates that the unsymmetrical form is favored.

Surprisingly, no reaction could be detected for the divinylmercury–dicyclopropylmercury redistribution after 2 weeks at 90°. The fact that no mixed mercury compounds could be detected must be due either to a very low exchange rate (kinetic control) or to the instability of the unsymmetrical product (thermodynamic control). Further study of this system involving isotopic labeling or a direct low-temperature synthesis of the mixed product would demonstrate whether the absence of unsymmetrical product was due to kinetic or thermodynamic control.

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