residue was dried over phosphorus pentoxide to give a transparent, colorless resin. Treatment with diethyl ether or ethanol did not induce crystallization. Structure VII is supported by phosphorus and nitrogen analysis, by its water solubility, and by strong infrared absorption at ~1220 cm.$^{-1}$ which is due to the P_3N_5 ring vibration.[7]

Anal. Calcd. for $C_{12}H_{36}N_9O_{18}P_3S_6$: N, 14.22; P, 10.56. Found: N, 14.11; P, 10.51.

2,2,4,4,6,6-Hexakis(N-β-mercaptoethylamido)cyclotriphosphaza-1,3,5-triene (VIII).—To a solution of 1 g. of I in 25 ml. of absolute ethanol, dry hydrogen sulfide was passed in until a crystalline colorless reaction product began to separate. The mixture was allowed to stand overnight; the solid formed (1.0 g.), m.p. 290° dec., was isolated by filtration. No solvent could be found for recrystallization of these crystals. Phosphorus and nitrogen values as well as the powerful absorption peak in the infrared spectrum at approximately 1220 cm.$^{-1}$ support structure VIII.[7]

Anal. Calcd. for $C_{12}H_{36}N_9P_3S_6$: N, 21.30; P, 15.70. Found: N, 20.99; P, 14.89.

2,2,4,4,6,6-Hexakis(N-β-thiophenylethylamido)cyclotriphosphaza-1,3,5-triene (IX).—A mixture of 3.87 g. of I (m.p. 153°, 0.01 mole) with 6.7 g. of benzenethiol (0.06 mole) was kept at 0° for about 1 hr. until solution was complete. The almost colorless highly viscous liquid reaction product was treated with two portions of 20 ml. of petroleum ether to remove unreacted benzenethiol. Crystallization could not be induced by treatment with various solvents or by refrigeration of a concentrated solution in carbon tetrachloride. Purification was achieved by precipitating the product from its solution in carbon tetrachloride with petroleum ether, dissolving the oil thus obtained in a small amount of ether, and again reprecipitating the oil by addition of petroleum ether. After decantation, the product was kept at 0.1 mm. pressure at 80° for 2 hr. to give a colorless viscous oil, $n^{30}D$ 1.6462.

Anal. Calcd. for $C_{48}H_{60}N_9P_3S_6$: C, 54.99; H, 5.77; N, 12.03; P, 8.86; S, 18.35. Found: C, 55.50; H, 6.50; N, 12.45; P, 8.90.

The infrared spectrum of this compound (Table I) is in agreement with structure IX.

2,2,4,4,6,6-Hexakis(N-β-benzoyloxyethylamido)cyclotriphosphaza-1,3,5-triene (X).—A solution of 3.87 g. of I (m.p. 153°, 0.01 mole) and 7.327 g. of benzoic acid (0.06 mole) in 100 ml. of chloroform was allowed to stand at ambient temperature for 1 week. The solvent was removed by vacuum distillation from the still clear and colorless solution. A highly viscous, colorless oil (12 g., calculated amount 11.2 g.) was obtained as a residue, which did not crystallize on treatment with various solvents or prolonged standing. Purification was attempted by dissolving the product in carbon tetrachloride and washing the solution several times with aqueous sodium bicarbonate. After drying over sodium sulfate, petroleum ether was added to the filtrate to result in precipitation of an oil. Decantation and removal of the adhering solvent at 80° (0.1 mm.) gave a colorless, extremely viscous oil. The infrared spectrum of this compound (Table I) is in agreement with structure X.

CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY,
CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI

Exchange Reactions and Nuclear Magnetic Resonance Analysis of Some Organomercury Compounds[1]

BY MARVIN D. RAUSCH[2] AND JOHN R. VAN WAZER

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The equilibrium compositions and reaction kinetics of several exchange reactions involving organomercury systems have been determined by means of proton n.m.r. spectroscopy. In systems involving either dimethylmercury or dibenzylmercury and mercuric chloride, bromide, or iodide, the corresponding organomercuric halide is the only product detectable at equilibrium, indicating a highly nonrandom exchange. The relative rates of reaction of dimethylmercury with mercuric halides in methanol at 36° decrease in the order $HgCl_2 > HgBr_2 > HgI_2$, although the relative rates in dioxane are in the order $HgBr_2 > HgCl_2 > HgI_2$. Dimethylmercury and diphenylmercury undergo an exchange reaction at 150° to produce an essentially random or statistical mixture of these mercurials and methylphenylmercury; disproportionation of the latter unsymmetrical compound at 100° produces the same result. Dibenzylmercury likewise undergoes exchange reactions with dimethylmercury and diphenylmercury on heating, although concomitant decomposition to bibenzyl and metallic mercury does not permit the equilibrium compositions to be ascertained. The proton n.m.r. spectra of a variety of organomercury compounds in solution have been determined, and many of these exhibit spin–spin coupling between Hg^{199} and adjacent protons. Exchange reactions involving bis(perfluoromethyl)mercury and bis(perfluorophenyl)mercury have been studied by means of F^{19} n.m.r.

Introduction

Nuclear magnetic resonance (n.m.r.) spectroscopy has proved to be a highly useful tool for the examination of chemical equilibria, since this technique permits the analysis of various species present without disruption of the conditions required for equilibrium.[3] It was of interest to determine if H^1 and F^{19} n.m.r. could be used to determine chemical equilibria and reaction kinetics in systems involving organomercury compounds. Since only a limited amount of information is presently available concerning the n.m.r. spectra of mercurials, a number of such spectra have been recorded and are examined in this paper.

Experimental

Materials.—Dimethylmercury and dibenzylmercury were obtained from Metallomer Laboratories, and diphenylmercury was obtained from Distillation Products Industries. Bis(perfluoromethyl)mercury and bis(perfluorophenyl)mercury were prepared

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[2] Department of Chemistry, University of Massachusetts, Amherst, Mass.

[3] J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).

according to published procedures.[4,5] Mercuric bromide and iodide were obtained from Matheson Coleman and Bell, while the mercuric chloride came from Allied Chemical Co. All mercuric salts were reagent grade. The methylmercuric halides and benzylmercuric halides were prepared by the reaction of the dialkylmercury with the appropriate mercuric halide in either methanol or ethanol for *ca.* 30 min., followed by cooling and crystallization of the product. All organomercuric halides were recrystallized from ethanol before use, and their melting points were in agreement with literature values. Matheson Coleman and Bell spectro-reagent grade dioxane and methanol were used without further purification. Deuteriochloroform was purchased from Volk Radiochemical Co. and was of *ca.* 99 atom % isotopic purity.

Methylphenylmercury was prepared by the reaction of methylmercuric chloride and phenyllithium in diethyl ether solution at 0°, followed by hydrolysis and removal of the solvent. Vacuum distillation of the reaction product resulted in extensive redistribution into dimethylmercury and diphenylmercury, although a small quantity (*ca.* 15%) of the desired product was obtained in the form of a heavy viscous oil, b.p. 70–72° (0.30 mm.).

Anal. Calcd. for C_7H_8Hg: C, 28.72; H, 2.75; mol. wt., 292.7. Found: C, 28.64; H, 2.84; mol. wt. (osmometric in benzene), 301, 304.

The elemental and molecular-weight analyses together with the proton n.m.r. spectrum of this material (Table III) are in agreement with its formulation as methylphenylmercury.

H^1 n.m.r. spectra were determined at 36° on a Varian Model A-60 spectrometer at a frequency of 60.000 Mc. Peaks are referenced to tetramethylsilane as an internal standard. F^{19} n.m.r. spectra were measured at 27° on a Varian Model HR-60 spectrometer at a frequency of 56.444 Mc. Peaks are referenced to trifluoroacetic acid as an external standard, using either the superposition technique or by calibration of the trace by the side-band method.

Dimethylmercury–Mercuric Halide Systems.—Dimethylmercury (0.231 g., 0.001 mole) and the appropriate mercuric halide (0.001 mole) were weighed separately into two 25-ml. glass-stoppered erlenmeyer flasks. Either dioxane (9.70 ml.) or methanol (9.70 ml.) was added to the flask containing the mercuric salt, and both flasks were thermostated at 36° (in the case of mercuric iodide and methanol, it was necessary to warm the flask to *ca.* 50° in order to totally dissolve the salt, after which the clear solution was cooled to 36°). The mercuric halide solution was quickly added to the flask containing the dimethylmercury, the contents were vigorously mixed for *ca.* 30 sec., an aliquot was added to a 5-mm. thin-wall precision-bore tube, and the tube was inserted into the n.m.r. probe maintained at 36.0 ± 0.3°. The concentrations of both dimethylmercury and the methylmercuric halide were obtained as a function of time by integration of the resonance maxima for the methyl protons of each compound. Since approximately 10–15 sec. was required to integrate both peaks, the mean integration time was recorded. Each reaction was followed to completion. All values reported are the average of two or more runs. Reproducibility was ±3% except for the reactions between dimethylmercury and either mercuric chloride or mercuric bromide in methanol, in which case the reproducibility was ±20%.

The intensity value representing dimethylmercury was halved in order to normalize for the number of protons present in dimethylmercury as compared to the methylmercuric halides. Since no other resonance maxima were noted in the spectra other than those due to dimethylmercury and the methylmercuric halides, the molar concentration of the mercuric halide was assumed to be equal to the concentration of dimethylmercury at any given time.

Dibenzylmercury–Mercuric Halide Systems.—The procedure was the same as outlined for the dimethylmercury studies, except that dibenzylmercury (0.383 g., 0.001 mole) was used. Integration proved difficult in these systems since the methylene resonance maxima occur very near to the resonance for dioxane. For this reason, only chemical shifts and equilibrium values were determined.

Dimethylmercury–Diphenylmercury System. A.—Dimethylmercury (0.231 g. 0.001 mole) and diphenylmercury (0.355 g., 0.001 mole) were weighed into 5 mm. by 16 cm. thick-walled Pyrex tubes. The latter had previously been flushed with nitrogen. The tubes were cooled in Dry Ice and sealed. Each tube was totally immersed in a bath of silicone oil maintained at 150 ± 2°. The tubes were occasionally removed for brief periods and vigorously shaken in order to ensure complete mixing. At appropriate intervals, they were withdrawn, quenched in Dry Ice, carefully opened, and the contents were dissolved in 0.4 ml. of deuteriochloroform. N.m.r. spectra were obtained and the resonance peaks due to the methyl protons of dimethylmercury and methylphenylmercury were integrated. Since no resonance maxima other than those due to these products were observed and no visual sign of decomposition was noted, it was concluded that the total molar concentrations of dimethyl and diphenyl groups on the mercury were always equal. From the normalized intensities, the mole per cents of dimethylmercury, diphenylmercury, and methylphenylmercury were calculated.

B.—Small quantities (*ca.* 0.15 g.) of methylphenylmercury (containing less than 1% dimethylmercury according to its n.m.r. spectrum) were weighed into glass tubes as outlined in method A. The tubes were sealed and totally submerged in a bath of silicone oil maintained at 100 ± 1°. At various intervals, the tubes were withdrawn and worked up as in method A. The mole per cents of dimethylmercury, diphenylmercury, and methylphenylmercury were calculated as before.

Dibenzylmercury–Dimethylmercury and Dibenzylmercury–Diphenylmercury Systems.—The procedures were the same as outlined in method A for the dimethylmercury–diphenylmercury system, except that 0.001 mole of dibenzylmercury and 0.001 mole of either dimethylmercury or diphenylmercury were employed. The exchange reactions were studied from 100 to 150°, and the products were again analyzed by proton n.m.r. spectroscopy.

Bis(perfluoromethyl)mercury–Mercuric Halide Systems.—Bis(perfluoromethyl)mercury (0.005 mole, 0.169 g.) and the appropriate mercuric halide (0.005 mole) were weighed into 5 mm. by 16 cm. thick-walled Pyrex tubes which had previously been flushed with nitrogen. The tubes were sealed and totally immersed in a bath of silicone oil maintained at 170 ± 5° for 4 hr. After this heating period, the reaction mixture was still only partially liquefied and a gray residue was noted. The tubes were withdrawn and quenched in Dry Ice. The contents of each tube was extracted with 0.8 ml. of methanol and filtered from the insoluble residue, and F^{19} n.m.r. spectra were obtained.

Bis(perfluoromethyl)mercury–Dimethylmercury, Bis(perfluoromethyl)mercury–Bis(perfluorophenyl)mercury, and Bis(perfluorophenyl)mercury–Dimethylmercury Systems.—The procedures were the same as outlined for the bis(perfluoromethyl)mercury–mercuric halide systems, except that 0.5-mmole portions of each respective reactant were employed. The tubes were heated at 150° for various time intervals and the contents of each tube after opening was extracted with 0.6 ml. of either deuteriochloroform or methanol. H^1 and/or F^{19} n.m.r. spectra were obtained.

Results and Discussion

Dialkylmercury–Mercuric Halide Exchanges.—The reaction between dialkyl- or diarylmercury compounds and mercuric halides has long been used as a convenient synthetic route to alkyl- or arylmercuric halides.[6]

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[4] H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2953 (1949).

[5] R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, *ibid.*, 4367 (1962).

[6] (a) F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), New York, N. Y., 1921, p. 65; (b) E. Krause and A. von Grosse, "Die Chemie der metall-organischen Verbindungen," Edward Bros. Inc., Ann Arbor, Mich., 1943, pp. 130, 149, 153 (photo-lithoprint reproduction); (c) H. Gilman, "Organic Chemistry—An Advanced Treatise," Vol. 1, 2nd Ed., John Wiley and Sons, New York, N. Y., 1943, p. 551.

The fact that high yields of organomercuric halides can frequently be obtained in this manner by crystallization from the reaction mixture has little bearing on the original equilibrium conditions, since the appearance of a heterogeneous crystalline phase could shift the equilibrium according to the principle of Le Chatelier. An earlier attempt to obtain equilibrium constants in these systems by conductance measurements was unsuccessful.[7]

Initial studies indicated that various methylmercuric halides in either dioxane or methanol solutions exhibited resonance peaks due to the methyl protons appreciably downfield from the corresponding peak for dimethylmercury. When equimolar amounts of dimethylmercury and a mercuric halide were combined in either solvent and allowed to stand at room temperature for several days, resonance absorption corresponding to the presence solely of the respective methylmercuric halide was observed, and dimethylmercury could no longer be detected. Dilute solutions of the reactants were employed in order to prevent crystallization of the methylmercuric halide. These results indicate that the mixed mercurials (the methylmercuric halides) exist in preponderant amounts in equilibrium mixtures with dimethylmercury and mercuric halides, and that the equilibrium constants in each case for eq. 1 must be very large ($>10^4$).

$$R_2Hg + HgX_2 \rightleftharpoons 2RHgX \qquad (1)$$

R = CH_3 or $CH_2C_6H_5$; X = Cl, Br, or I

These findings are in good agreement with the large K values calculated from thermochemical data[8] on the basis that the entropy contribution to the free energy is solely attributable to randomization.[3] Thus, for eq. 1 in ethanol with $R = CH_3$ and $X = Cl$, $K = 3.5 \times 10^{11}$; with $R = CH_3$ and $X = Br$, $K = 2.5 \times 10^9$. In methanol with $R = CH_3$ and $X = I$, $K = 3.4 \times 10^5$.

Equilibrium studies also were made employing dibenzylmercury and mercuric halides in dioxane solution (benzylmercuric halides are only very slightly soluble in methanol at 36°). In these studies, resonance peaks for the methylene protons in dibenzylmercury and the benzylmercuric halides served as a convenient means of analysis. After several days standing, only the respective benzylmercuric halide could be detected at equilibrium, indicating that the equilibrium constants in these systems must also be very large (eq. 1, $R = CH_2C_6H_5$; X = Cl, Br, or I).

The chemical kinetics for the reaction between dimethylmercury and a mercuric halide in either dioxane or methanol solution could also be determined by means of proton n.m.r. spectroscopy. The concentrations of both dimethylmercury and the methylmercuric halide could conveniently be followed as a function of time by repeated integration of the methyl proton resonance absorptions. A plot of $1/[(CH_3)_2Hg]$ *vs.* time yielded a satisfactory straight line in each case, in agreement with the second-order kinetics observed previously for these systems in dioxane,[9] ethanol,[9,10] and acetone.[10] The rate data obtained for these reactions are presented in Table I, together with some related data from the studies of Dessy and co-workers.[9]

TABLE I

SECOND-ORDER RATE CONSTANTS (L./MOLE-SEC.) AT 36° FOR THE REACTION

$$R_2Hg + HgX_2 \xrightarrow{\text{solv.}} 2RHgX$$

R	X	In dioxane	In methanol
CH_3	Cl	0.00259	1.05
CH_3	Br	0.00354	0.30
CH_3	I	0.00154	0.0505
C_2H_5	I	0.0320^a	. . .
C_6H_5	I	3.90^a	$1.13 \times 10^{2a,b}$

[a] Spectrophotometric data at 35° from ref. 9. [b] In ethanol.

A comparison of the rate data obtained in the present study with that of Dessy and co-workers reveals several interesting features. First, the relative rate of reaction of dimethylmercury and mercuric iodide is approximately 33 times faster in methanol than in dioxane as the solvent at 36°. Dessy and co-workers have observed a strikingly similar 29-fold increase in the relative reaction rate of diphenylmercury and mercuric iodide in ethanol compared to dioxane. Second, in agreement with earlier findings, the second-order rate constant for the reaction of dimethylmercury and mercuric iodide in dioxane solution is appreciably lower than similar constants obtained for the reactions of other homologous dialkylmercury compounds and this salt. Third, in contrast to the relative rates of reaction of dimethylmercury in methanol (which proceed in the decreasing order $HgCl_2 > HgBr_2 > HgI_2$), the relative reaction rates in dioxane exhibit the partially inverted sequence $HgBr_2 > HgCl_2 > HgI_2$. Dessy and co-workers have observed that in reactions of diphenylmercury and mercuric halides in dioxane, the sequence of reactivity appears to be $HgCl_2 > HgBr_2 > HgI_2$, and that this reactivity sequence is approximately the same as the order of decreasing ionic character of the mercury–halogen bond.

Dimethylmercury–Diphenylmercury Exchange.—It was of additional interest to use proton n.m.r. spectroscopy as a means of examining equilibrium mixtures of various dialkyl- or diarylmercury compounds. Only one such study involving the equilibrium established between two organomercury compounds of the type R_2Hg has previously been described.[11,12]

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[7] I. B. Johns, W. D. Peterson, and R. M. Hixon, *J. Phys. Chem.*, **34**, 2218 (1930).

[8] K. Hartley, H. O. Pritchard, and H. A. Skinner, *Trans. Faraday Soc.*, **46**, 1019 (1950).

[9] R. E. Dessy and Y. K. Lee, *J. Am. Chem. Soc.*, **82**, 689 (1960); R. E. Dessy, Y. K. Lee, and J. Y. Kim, *ibid.*, **83**, 1163 (1961).

[10] H. B. Charman, E. D. Hughes, and C. Ingold, *J. Chem. Soc.*, 2523, 2530 (1959).

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

[12] Isotope exchange between molecules of symmetrical organomercury compounds has recently been reported, *viz.*

$$[p\text{-}(CH_3)_2NC_6H_4]_2Hg + (C_6H_5)_2Hg^{203} \rightleftharpoons [p\text{-}(CH_3)_2NC_6H_4]_2Hg^{203} + (C_6H_5)_2Hg$$

Mixed mercurials of the typeRHg R′ were apparently not observed in these studies.

Calingaert and co-workers[11] observed that both methylethylmercury and an equimolar mixture of dimethylmercury and diethylmercury gave an essentially random mixture of the three mercurials when allowed to stand at room temperature in the presence of aluminum chloride as a catalyst. The catalyst presumably forms a loose complex with the dialkylmercury and thus assists redistribution of the alkyl groups around mercury to occur.[13] The quantities of the organomercury compounds present at equilibrium were determined by analytical distillation.

In the present studies, equimolar amounts of dimethylmercury and diphenylmercury were heated in the absence of a catalyst under nitrogen in sealed tubes maintained at *ca.* 150°. At various time intervals, the tubes were removed, opened, the contents dissolved in deuteriochloroform, and proton n.m.r. spectra obtained. A resonance peak attributable to the methyl protons of the unsymmetrical organomercury compound, methylphenylmercury, was noted at *ca.* 0.28 p.p.m. downfield from the resonance peak for dimethylmercury (Table II).

TABLE II

H^1 N.M.R. SPECTRA OF SOME ORGANOMERCURY COMPOUNDS

Compound	Group	Chemical shifts, p.p.m.[a]	Concn. and solvent	$J_{H^1-Hg^{199}}$, c.p.s.
$(CH_3)_2Hg$	CH_3	−0.32	Neat	101[b]
$(CH_3)_2Hg$	CH_3	−0.19	10% in dioxane	103
$(CH_3)_2Hg$	CH_3	−0.27	10% in $CDCl_3$	101
$(CH_3)_2Hg$	CH_3	−0.22	5% in methanol	104
CH_3HgCl	CH_3	−0.84	10% in dioxane	209
CH_3HgCl	CH_3	−0.93	5% in methanol	212
CH_3HgBr	CH_3	−0.91	10% in dioxane	205
CH_3HgBr	CH_3	−0.99	5% in methanol	207
CH_3HgI	CH_3	−0.98	10% in dioxane	...
CH_3HgI	CH_3	−1.05	5% in methanol	...
$CH_3HgC_6H_5$	CH_3	−0.55	10% in $CDCl_3$	109
$CH_3HgC_6H_5$	C_6H_5	−7.30[c]	10% in $CDCl_3$	...
$(C_6H_5)_2Hg$	C_6H_5	−7.35[c]	10% in $CDCl_3$	...
$(C_6H_5CH_2)_2Hg$	CH_2	−2.37	10% in $CDCl_3$	133
$(C_6H_5CH_2)_2Hg$	C_6H_5	−6.97, −7.02[c]	10% in $CDCl_3$	...
$(C_6H_5CH_2)_2Hg$	CH_2	−2.32	10% in dioxane	138
$(C_6H_5CH_2)_2Hg$	C_6H_5	−7.03, −7.01[c]	10% in dioxane	...
$C_6H_5CH_2HgCl$	CH_2	−3.07	10% in dioxane	271
$C_6H_5CH_2HgCl$	C_6H_5	−7.17[c]	10% in dioxane	...
$C_6H_5CH_2HgBr$	CH_2	−3.11	10% in dioxane	266
$C_6H_5CH_2HgBr$	C_6H_5	−7.17[c]	10% in dioxane	...
$C_6H_5CH_2HgI$	CH_2	−3.14	10% in dioxane	...
$C_6H_5CH_2HgI$	C_6H_5	−7.16	10% in dioxane	...

[a] Referenced to tetramethylsilane as an internal standard, using a Varian A-60 spectrometer. All chemical shifts are accurate to within ±0.02 p.p.m., and coupling constants to within ±1 c.p.s. [b] Reported: 102 c.p.s. (R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959)). [c] Chemical shift of the most intense peak of a series.

A state of equilibrium in this system was reached in *ca.* 6 hr. at 150° (eq. 2). Equilibrium could also be attained at 100°, although much longer time

$$(CH_3)_2Hg + (C_6H_5)_2Hg \rightleftharpoons 2CH_3HgC_6H_5$$

$$K = [CH_3HgC_6H_5]^2/[(CH_3)_2Hg][(C_6H_5)_2Hg] \qquad (2)$$

periods (*ca.* 80 hr.) were required. As in Calingaert's study, nearly random distribution of the three organomercury compounds was observed.

In order to provide a further check on the equilibrium composition of this system, methylphenylmercury was prepared and studied. This unsymmetrical organomercury compound has been described several times in the literature,[14] although the purity of the product in each instance appears questionable. Methylphenylmercury was prepared in the present study by the reaction of methylmercuric chloride and phenyllithium at 0°, followed by hydrolysis and distillation. The product was identified by elemental, molecular weight, and n.m.r. analyses. Small portions of methylphenylmercury rapidly underwent disproportionation when heated at 100°, and a state of equilibrium was reached in *ca.* 30 min. The compositions of the equilibrium mixtures, as determined by n.m.r. analysis, indicated an essentially random distribution of methylphenylmercury, dimethylmercury, and diphenylmercury in these mixtures as well. From the analysis of twenty equilibrium compositions starting with both the unsymmetrical mercurial and a 50–50 mixture of the pair of symmetrical mercurials, the weighted-average equilibrium constant for eq. 2 was calculated to be 4.4 ($K_{random} = 4.0$) with a standard deviation of 0.8. Thus, the observed constant does not significantly differ from randomness.

Dibenzylmercury–Dimethylmercury and Dibenzylmercury–Diphenylmercury Exchanges.—When equimolar quantities of dibenzylmercury and diphenylmercury were heated in sealed tubes at 150°, proton n.m.r. analysis of the resulting products indicated a resonance peak attributable to the methylene protons of benzylphenylmercury at *ca.* 0.20 p.p.m. ($J_{H^1-Hg^{199}}$ = 140 c.p.s.) downfield from the corresponding resonance peak for dibenzylmercury. A second resonance peak due to bibenzyl appeared at *ca.* −2.80 p.p.m. and the intensity of this peak increased as the period of heating increased. Concurrently with bibenzyl formation, equivalent amounts of metallic mercury were noted. Both dibenzylmercury[15] and benzylphenylmercury[16] are reported to decompose to bibenzyl on heating. In the present studies, no resonance peak attributable to diphenylmethane (which could result from mercury elimination in benzylphenylmercury and concomitant unsymmetrical coupling) was observed.

Under the experimental conditions employed, the rate of mercury elimination was slow in comparison to the rate of exchange so that the amount of benzylphenylmercury maximized at *ca.* 40 hr. at 120°. From the stoichiometry at this maximum, the equilibrium constant of the form of eq. 2 is estimated to be between 2.7 and 3.8—a value slightly less than but obviously not statistically different from that expected for a random distribution.

Equimolar quantities of dibenzylmercury and dimethylmercury likewise exhibited an exchange reaction

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[13] G. Calingaert and H. A. Beatty, "Organic Chemistry—An Advanced Treatise," H. Gilman, Ed., Vol. 2, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1806.

[14] M. S. Kharasch and R. Marker, *J. Am. Chem. Soc.*, **48**, 3130 (1926); R. C. Freidlina, A. N. Nesmeyanov, and K. A. Kocheshkov, *Ber.*, **66B**, 365 (1935); M. M. Koton and A. A. Bol'shakova, *Zh. Obshch. Khim.*, **23**, 2023 (1953); A. A. Bol'shakova, *ibid.*, **24**, 266 (1954).

[15] P. Wolff, *Ber.*, **46**, 64 (1913).

[16] S. Hilpert and G. Gruttner, *ibid.*, **48**, 906 (1915).

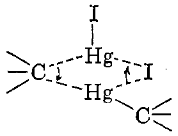
to produce benzylmethylmercury. The latter compound was characterized by a methyl proton resonance peak at *ca.* 0.07 p.p.m. ($J_{H^1-Hg^{199}}$ = 106 c.p.s.) downfield from the resonance peak for dimethylmercury, and a methylene proton resonance peak at *ca.* 0.09 p.p.m. ($J_{H^1-Hg^{199}}$ = 130 c.p.s.) upfield from the corresponding peak for dibenzylmercury. The intensities of the methyl and methylene proton resonances were in the ratio of 3:2. As in the dibenzylmercury–diphenylmercury system, a proton resonance at −2.80 p.p.m. due to bibenzyl was noted and ethylbenzene was not detected. Again, metallic mercury was formed. In view of the complexity of the n.m.r. spectra, no attempt was made to estimate the equilibrium constant.

Proton N.m.r. Spectra.—The proton n.m.r. spectra of organomercury compounds are particularly interesting for study, since the naturally occurring Hg^{199} isotope (16.9% natural abundance) has a nuclear spin of $^1/_2$. Because of the presence of Hg^{199}, the proton resonance peaks of many organomercury compounds should be accompanied by smaller, symmetrically disposed satellite peaks which result from spin–spin coupling of Hg^{199} and the protons. Satellite peaks of this type have previously been observed in several dialkylmercury compounds determined as neat liquids.[17,18]

The proton resonance data for a variety of organomercury compounds in various solvents are summarized in Table II. In addition to confirming the spin–spin coupling of the methyl protons with Hg^{199} in dimethylmercury, much weaker symmetrically disposed satellite peaks attributable to spin–spin coupling of the protons with C^{13} (spin = $^1/_2$, natural abundance = 1.1%) were observed ($J_{H^1-C^{13}}$ = 130 c.p.s.). This value for the coupling constant between C^{13} and the protons in dimethylmercury is similar to values reported for C^{13}–H^1 spin–spin coupling in other compounds.[19]

In all the alkylmercury compounds described above with the exception of methyl- and benzylmercuric iodides, satellite peaks due to spin–spin coupling of the methyl or methylene protons with Hg^{199} were observed. The pre-exchange lifetimes for carbon–mercury linkages in solution must in general be reasonably long.[20]

The absence of spin–spin coupling in compounds of the type RHgI is striking. A possible explanation could be that there is rapid exchange of methyl groups between Hg^{199} and other mercury isotopes in solutions of organomercuric iodides.



This explanation is supported by the finding that the addition of iodide ion (in the form of either sodium iodide or mercuric iodide) to a solution of methylmercuric chloride in either dioxane or methanol solution resulted in collapse of the H^1–Hg^{199} doublets.

As might be anticipated, substitution of a halogen for the less electronegative methyl group in methylmercuric halides results in an appreciable downfield shift of the resonance peak due to the methyl protons. The same effect is observed for the methylene protons in benzylmercuric halides as compared to dibenzylmercury. Among the alkylmercuric halides in both series, however, the order of chemical shifts to lower fields is RHgI > RHgBr > RHgCl. This result is the reverse of the trend expected on the basis of electronegativity effects alone. In this regard, Hg^{199} n.m.r. studies on mercuric halides and anions of the type $[HgX_4]^{-2}$ have shown that shielding of the mercury decreases as the electronegativity of the halogen and the ionic character of the mercury–halogen bond increase.[21] Similar apparent reversals of electronegativity effects have been found in proton n.m.r. studies involving the methyl and methylene proton resonance shifts in ethyl halides,[22] in C^{13} n.m.r. studies involving C^{13} directly attached to halogens as well as C^{13} one atom removed from halogens,[19] and in the series of trimethylsilicon halides.[23]

Mixtures of equal amounts (by weight) of methylmercuric chloride, bromide, and iodide in either methanol or dioxane were found to produce a single sharp proton resonance peak, and the chemical shift of this peak was very nearly the value for methylmercuric bromide alone. A similar sharp methylene proton resonance peak was found when mixtures of the benzylmercuric halides were combined in dioxane. These results indicate rapid exchange of the halogens of organomercuric halides in solution.

Systems Involving Bis(perfluoromethyl)mercury and Bis(perfluorophenyl)mercury.—The F^{19} n.m.r. spectra of both bis(perfluoromethyl)mercury and bis(perfluorophenyl)mercury are summarized in Table III. In analogy to the H^1 n.m.r. spectrum of dimethylmercury, the F^{19} n.m.r. spectrum of bis(perfluoromethyl)mercury in a variety of solvents exhibits a single resonance peak accompanied by symmetrically disposed satellites due to spin–spin interaction of the fluorine nuclei with Hg^{199}. The fact that spin–spin coupling is observed for this mercurial in various solutions indicates that the pre-exchange lifetime for the perfluoromethyl–mercury bond is relatively long. Coupling interaction of this type is also consistent with the suggestion that the remarkable solubility of bis(perfluoromethyl)mercury in aqueous solution is not

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[18] P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 34 (1960).

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[20] A similar conclusion has been reached by others: R. E. Dessy, F. Kaplan, G. R. Coe, and R. M. Salinger, *J. Am. Chem. Soc.*, **85**, 1191 (1963).

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TABLE III

F^{19} N.M.R. SPECTRA OF SOME ORGANOMERCURY COMPOUNDS

Compound	Chemical shifts, p.p.m.[a]	Concn. and solvent	$J_{F^{19}-Hg^{199}}$, c.p.s.
$(CF_3)_2Hg$	−41.59 (±0.01)	10% in H_2O	1324.0 (±1.0)
$(CF_3)_2Hg$	−40.21 (±0.01)	10% in CH_3OH	1323.0 (±1.0)
$(CF_3)_2Hg$	−42.72 (±0.01)	14% in $CDCl_3$	1253.0 (±2.0)
$(CF_3)_2Hg$	−42.00 (±0.01)	10% in C_6H_6	1259.0 (±2.0)
$(C_6F_5)_2Hg$	+40.87 (±0.01), +71.76 (±0.02), +80.20 (±0.01)[b]	26% in $CDCl_3$	416.0 (±5.0)
$(C_6F_5)_2Hg$	+42.64 (±0.02), +78.11 (±0.02), +84.67 (±0.01)[b]	25% in CH_3OH	454.0 (±5.0)

[a] Referenced to trifluoroacetic acid as an external standard using a Varian HR-60 spectrometer. [b] Values given are for the centers of the multiplets.

due to ionization into mercuric and perfluoromethyl ions.[4,24]

The F^{19} n.m.r. spectrum of bis(perfluorophenyl)mercury in methanol solution exhibits three multiplet resonances. The multiplet at lowest field is surrounded by two small, symmetrically disposed satellite multiplets and is therefore assigned to the *ortho* fluorine nuclei. The multiplet at +78.11 p.p.m. has half the area of either the low or high field multiplet and appears as a triple triplet ($J_{F-F} \cong 20$ c.p.s.; $J_{F-F} \cong 2$ c.p.s.). Because of its area and splitting pattern, it is assigned to the *para* fluorine nuclei. The resonance at highest field is thus assigned to the *meta* fluorines. The spectrum of bis(perfluorophenyl)mercury in deuteriochloroform solution is very similar. A more detailed analysis of the n.m.r. spectra of compounds containing the perfluorophenyl group is in progress and will be reported later.

Because of the relatively high electronegativity of perfluoroalkyl and -aryl groups and the suggestion that they are "pseudo halogens,"[24] it was of interest to study exchange reactions involving perfluorinated mercurials and to compare the resulting kinetics and equilibria with results for the corresponding hydrocarbon analogs. However, in all studies involving the heating of bis(perfluoromethyl)mercury at 150° either with or without a solvent, partial decomposition into gaseous products and insoluble residues resulted and prevented quantitative equilibrium and rate measurements. On the other hand, the formation of exchange products could be readily ascertained *via* F^{19} n.m.r.

The methanol-soluble products of the reaction of equimolar amounts of bis(perfluoromethyl)mercury and mercuric chloride at 170° gave the F^{19} n.m.r. spectrum having a peak at −40.68 (±0.01) p.p.m. [$J_{F-Hg^{199}}$ = 1321 (±1) c.p.s.] due to the starting mercurial and a peak at −44.97 (±0.01) p.p.m. attributable to perfluoromethylmercuric chloride. Perfluoromethylmercuric bromide [−44.67 (±0.01) p.p.m.; $J_{F-Hg^{199}}$ = 1928 (±1) c.p.s.] and perfluoromethylmercuric iodide [−43.38 (±0.01) p.p.m.; $J_{F-Hg^{199}}$ = 1769 (±5) c.p.s.] were prepared and analyzed analogously. The appearance of F–Hg^{199} satellites in perfluoromethylmercuric iodide is in contrast to the results obtained for methylmercuric iodide (*vide supra*), although the satellite resonances appeared somewhat broadened compared to corresponding peaks in the spectra of perfluoromethylmercuric chloride and bromide. Attempts to carry out precise rate studies for these systems at 150° in methanol were not successful due to concomitant decomposition of the reaction product, although qualitatively the exchange between bis(perfluoromethyl)mercury and mercuric halides is enormously slower than for the corresponding exchanges involving dimethylmercury.

Exchange between bis(perfluoromethyl)mercury and dimethylmercury occurred slowly at 150°. The H^1 n.m.r. spectrum of the reaction products exhibited a peak at −0.28 p.p.m. [$J_{H^1-Hg^{199}}$ = 102 c.p.s.] due to dimethylmercury and a peak at −0.56 p.p.m. [$J_{H^1-Hg^{199}}$ = 139] attributable to methylperfluoromethylmercury. The corresponding F^{19} n.m.r. spectrum of the reaction products exhibited a peak at −42.8 p.p.m. [$J_{F-Hg^{199}}$ = 1250 c.p.s.] and a resonance at −41.1 p.p.m. [$J_{F-Hg^{199}}$ = 932 c.p.s.]. These resonances are assigned to bis(perfluoromethyl)mercury and methylperfluoromethylmercury, respectively.

The exchange reaction between bis(perfluoromethyl)mercury and bis(perfluorophenyl)mercury produced the mixed product, perfluoromethylperfluorophenylmercury. In addition to high-field peaks due to the ring fluorines, the F^{19} n.m.r. spectrum of the reaction products in methanol solution exhibited a peak at −40.47 (±0.01) p.p.m. [$J_{F-Hg^{199}}$ = 1322 (±1) c.p.s.] and a triplet of nearly identical chemical shift at −40.53 (±0.02) p.p.m. The former resonance is assigned to bis(perfluoromethyl)mercury and the latter to the mixed mercurial. The triplet pattern [J = 0.71 (±0.10) c.p.s.] of perfluoromethylperfluorophenylmercury is conceivably due to long-range spin–spin interaction between the methyl fluorines and the two equivalent *ortho* fluorines of the perfluorophenyl ring.

The reaction of equimolar amounts of bis(perfluorophenyl)mercury and dimethylmercury at 150° produced a clear homogeneous melt which was completely soluble in deuteriochloroform on cooling. The H^1 n.m.r. spectrum of the reaction products exhibited a very weak peak due to dimethylmercury at −0.29 p.p.m., a strong resonance attributable to methylperfluorophenylmercury at −0.89 p.p.m., and a weak resonance (~8% of total resonance) of unknown assignment (methylmercuric fluoride ?) at −1.17 p.p.m. A state of equilibrium was attained in *ca.* 1 hr. at 150°. On the basis of the dimethylmercury (3%) and methylperfluorophenylmercury (89%) present at equilibrium, it is evident that the exchange is highly nonrandom with $K > 2 \times 10^3$. The enhanced thermal stability and lack of disproportionation reactions observed by other workers[5] for methylpentafluorophenylmercury is thus accounted for.

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