Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ORGANOMETALLIC EXCHANGE REACTIONS
VIII. EXCHANGES IN MIXTURES OF METHYLMERCURY HALIDES AND PSEUDOHALIDES

L. L. MURRELL AND THEODORE L. BROWN
Wm. A. Noyes Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

(Received January 23rd, 1968)

SUMMARY

The rapid exchange of methyl groups between magnetically distinct sites in CH_3HgX/CH_3HgCN mixtures in dimethylformamide (DMF) has been shown to proceed with second-order kinetics, and may involve formation of a four-center, bridged transition state. The thermodynamic parameters for the exchange are strongly dependent on halide X. The Arrhenius activation energies are 22, 15 and 9 kcal/mole for I, Cl and Br, respectively. Corresponding entropies of activation are $+4$, -18 and -25 cal/deg·mole.

The exchanges in DMF are catalyzed slightly by mercuric halides, very markedly by tetramethylammonium bromide or iodide. Exchanges in pyridine are much faster than in DMF. The order of rates in CH_3HgX/CH_3HgCN mixtures in pyridine is in the order $X = Cl > Br \approx I$. Catalytic effects which are apparently due to reaction with solvent are noted. Species of the form $[C_5H_5NHgCH_3]^+X^-$ may be involved.

INTRODUCTION

The nature of the broadening of the ^{199}Hg–^1H coupled resonances in the PMR spectrum of methylmercury iodide has recently been discussed[1–3], and an earlier discussion of the nature of this effect corrected[4–6]. Binary mixtures of equal amounts of methylmercury chloride, bromide, or iodide show a single resonance at room temperature, at a chemical shift which is an average of the chemical shifts of the two component resonances, in dioxane and methanol[6]. The exchange averaging of the chemical shifts could be a result of either rapid methyl group and/or halide group exchange between the mercury species in solution. The presence or absence of ^{199}Hg–^1H scalar coupling in the mixed systems should reveal whether the Hg–C bond is labile.

Hatton *et al.* reported[5] a limited investigation of the ^{199}Hg–^1H scalar coupling of some mixed systems in pyridine solution at room temperature. They observed that the ^{199}Hg–^1H scalar coupling is *not* obliterated in the mixed systems. Rather, the single resonance observed exhibits an averaging in both the line width and chemical shift seen in the fast exchange limit. These results are compatible with halide, but not methyl group exchange in the mixed systems.

In this paper we report an investigation of the intermolecular exchange of halide and pseudohalide groups between different methylmercury halides. The results show that X and Y group exchange in CH_3HgX/CH_3HgY systems, in both DMF and pyridine, proceeds by a second-order pathway. The effect of the X and Y groups on the exchange pathway is discussed. The catalytic effects of mercuric halides and tetramethylammonium bromide and iodide on the exchange are also discussed.

EXPERIMENTAL

Materials and procedures

All operations were performed in a glove box under an argon atmosphere. Concentrations of methylmercury halides in solution were determined by integration of NMR peak areas using a compensating planimeter. 1 *M* stock solutions were prepared using accurately weighed samples of the halides or pseudohalides diluted to the appropriate volumes using calibrated syringes.

Methylmercury iodide and bromide were obtained from K and K Laboratories, methylmercury chloride from Columbia Organic Chemical Co., mercuric bromide and iodide from Baker Chemical Co., and tetramethylammonium bromide and iodide from Matheson, Coleman, and Bell Chemical Co. Methylmercury cyanide was obtained from sublimed methylmercury iodide and excess silver cyanide in the minimum volume of ethanol as discussed elsewhere[6], except that an inert atmosphere was maintained during reflux. All methylmercury compounds used were purified by repeated sublimations. Purity was checked by NMR. Satisfactory elemental analyses for halide and mercury were obtained for CH_3HgI and CH_3HgBr.

Dimethylformamide (DMF) was obtained from Baker Chemical Co. and distilled under an argon atmosphere after storage over Linde 4A molecular sieves. Spectral-grade pyridine obtained from Mallinkrodt Chemical Co. was refluxed under an inert atmosphere for at least four h over either potassium hydroxide or freshly heated barium oxide, and distilled under an argon atmosphere. Toluene was passed through a silica gel column, distilled, and stored over sodium wire in an inert atmosphere box.

Measurements of NMR spectra were made in the manner previously reported[7]. Samples were thoroughly degassed and sealed under vacuum in standard size NMR tubes.

Interpretation of NMR data

The reciprocal mean lifetime of halide groups between exchanges, $1/\tau_e$, was estimated by examination of the individual line widths in the region of slow exchange. Under the condition of slow exchange, the resonances are broadened; the line width is related to the mean lifetime (τ_j) by the expression

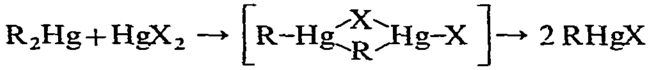
$$1/\tau_j = \pi(\Delta - \Delta^\circ)$$

where Δ° is the measured half-intensity width for the *j*th component in the absence of exchange[8]. This procedure is valid provided the broadening is not large enough to cause appreciable overlap of the signals. It is sometimes possible to determine the form of the rate law by evaluating the dependence of the individual τ_A and τ_B values on concentrations in the region of slow exchange. The slow exchange condition is defined such that the τ_j's are large compared to the reciprocal of the difference in chemical shifts of the two species.

RESULTS AND DISCUSSION

Exchanges in dimethylformamide

Dessy and coworkers[9] have shown the reactions

 (1)

$$R_2Hg+HgX_2 \rightarrow \left[R\text{-}Hg\overset{X}{\underset{R}{\rightleftarrows}}Hg\text{-}X\right] \rightarrow 2\,RHgX \qquad (1)$$

to be first order each in dialkylmercury and mercuric halide. Variation in the alkyl group has little effect on the activation energy, but variation in the halide has a marked effect. The sequence of reactivities was observed to be $HgCl_2 > HgBr_2 > HgI_2$, paralleling the decrease in ionic character of the Hg–X bond. Van Wazer and Rausch[6] similarly obtained second-order kinetics for the reaction of dimethylmercury with mercuric halide. It is noteworthy that in dioxane they obtained partial inversion of the sequence of the halide reactivities with a rate order $HgBr_2 > HgCl_2 > HgI_2$. The reaction of dialkylmercury with mercuric halide exhibits the characteristics of a second-order process associated with a bimolecular, four-center transition state.

A bimolecular reaction involving *only* bridging halides in the proposed four-center transition state should be particularly sensitive to the halide groups in the "bridging" positions. The thermodynamic parameters for methyl group exchange between the magnetically distinct sites in the systems CH_3HgCl/CH_3HgCN, CH_3HgBr/CH_3HgCN, and CH_3HgI/CH_3HgCN in dimethylformamide (DMF) (Table 1) are in harmony with this expectation. The Arrhenius plots for these systems are displayed in Fig. 1. Representative spectra for the CH_3HgI/CH_3HgCN system are shown in Fig. 2.

TABLE 1

THERMODYNAMIC PARAMETERS FOR EXCHANGE IN CH_3HgX/CH_3HgY SYSTEMS IN DMF

System	E_a[a]	E_a[b]	$\Delta S^{\neq}$[c]
CH_3HgI/CH_3HgCN	22±2	20±2	+4±3
CH_3HgCl/CH_3HgCN	15±2	15±2	−18±3
CH_3HgBr/CH_3HgCN	9±1	10±1	−25±2

[a] From log $1/\tau(CH_3HgX)$ *vs.* $1/T$ (kcal/mole). [b] From log $1/\tau(CH_3HgCN)$ *vs.* $1/T$ (kcal/mole).
[c] $k_f = \frac{kT}{h}\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT)$, where $\Delta H^{\neq} = E_a - RT$; $\Delta S^{\neq}$ in cal/deg·mole.

It is clear from the spectra obtained in this work, as well as those reported earlier, that the exchange process involves transfer of a halide or pseudohalide group, and not carbon–mercury bond rupture. If the latter process were occurring the ^{199}Hg–^{1}H scalar coupling would be obliterated in the pure components or mixed CH_3HgX/CH_3HgY systems. The broadening of the doublet due to components of the ^{199}Hg–^{1}H coupling in CH_3HgI[1-6], which we have also observed at all temperatures studied, has been ascribed to quadrupolar relaxation effects of the iodine nucleus[1-3].

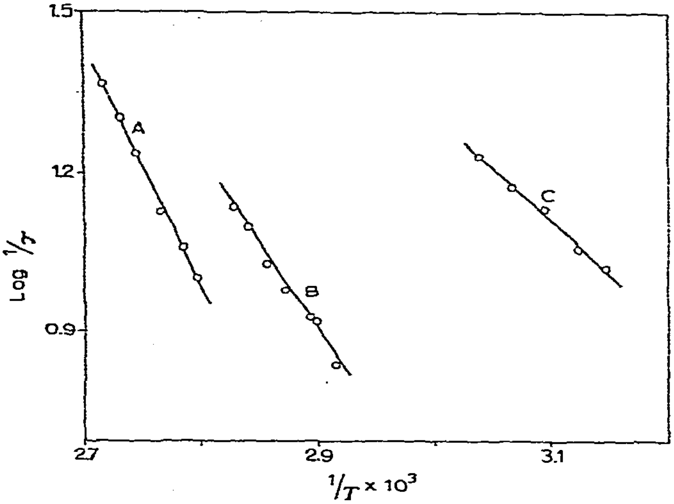


Fig. 1. Arrhenius plots of $1/\tau$ for methyl group exchanges in CH_3HgCN/CH_3HgX systems in dimethyl formamide. Lines A, B and C correspond to X = I, Cl and Br, respectively.

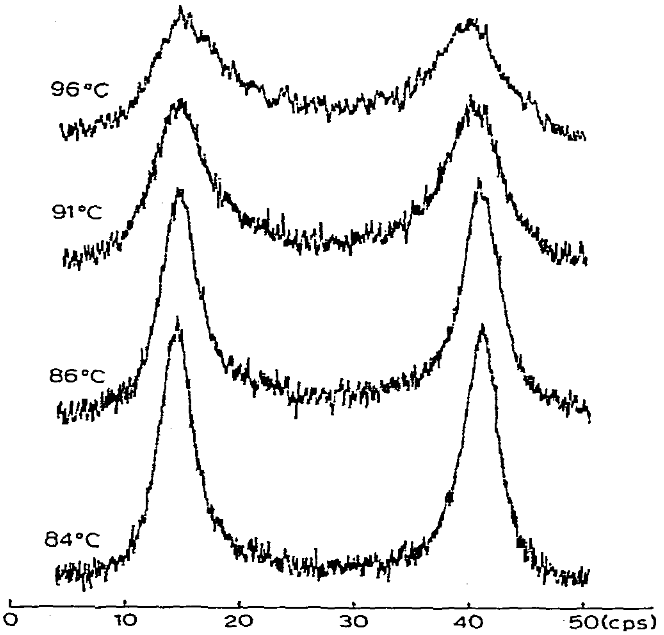


Fig. 2. Proton resonance spectra for a solution 0.5 *M* each in CH_3HgI and CH_3HgCN in DMF at various temperatures. It should be noted that the system contains six different sites, because of the presence of ^{199}Hg. Only the two sites involving non-spin-coupled protons are shown.

The observation that the ^{199}Hg–^1H coupling of a mixture of methylmercury iodide and another halide is an *average*, in both line-width and coupling constant, of the values characteristic of the pure components, is compatible with halide exchange, but not with methyl group exchange. It thus appears in general that the mercury–alkyl bond is not labile on the NMR time scale[10] (vinylmercury bromide[4], allylmercury bromide $+HgBr_2$[11], and dimethylmercury$+AlCl_3$[2] are apparent exceptions). As an illustration, the line-widths and coupling constants of the pure components and of the mixtures of CH_3HgX and CH_3HgCN in pyridine/toluene solvent at 35° are given in Table 2. The line-widths of the spin-coupled components exhibit no appreciable broadening, proof that the methylmercury bond is not rapidly broken.

TABLE 2

CHEMICAL SHIFTS, ^{199}Hg–^{1}H COUPLING CONSTANTS AND HALF-INTENSITY LINE-WIDTHS FOR CH_3HgX SYSTEMS

System	Central line-width (Hz)	Width of spin coupled line (Hz)	$J(^{199}Hg$–$^{1}H)$	δ^a
CH_3HgCN	0.5	0.6	176.9	97.1
CH_3HgBr	0.5	0.8	208.1	82.7
CH_3HgI	0.5	11[b]	203±2	77.4
0.5 *M* CH_3HgBr/ 0.5 *M* CH_3HgCN	0.7	0.6	193.3	89.8
0.5 *M* CH_3HgI/ 0.5 *M* CH_3HgCN	0.6	~6	187±2	87.9

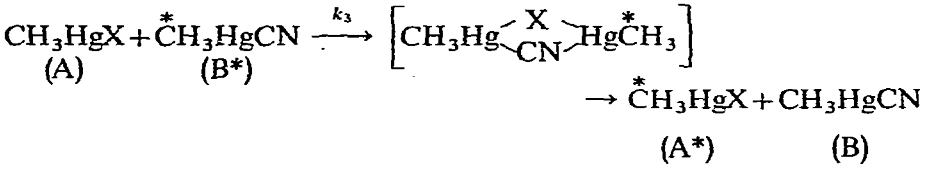
[a] From methyl resonance of toluene, in a 1 : 1 by volume pyridine/toluene mixture, in Hz. [b] Ref. 6.

TABLE 3

CONCENTRATION-VARIATION DATA FOR CH_3HgX/CH_3HgCN EXCHANGES IN DMF SOLUTION

Concentration of CH_3HgX (*M*)	Concentration of CH_3HgCN (*M*)	$1/\tau(CH_3HgX)$	$1/\tau(CH_3HgCN)$
X=I, 90°			
0.48	0.52	16.4	16.4
0.22	0.24	8.2	8.4
0.12	0.094	5.5	6.4
0.55	0.24	8.1	15.7
0.44	0.15	6.0	17.7
0.24	0.44	17.7	8.7
0.13	0.46	~24	6.9
X=Cl, 78°			
0.50	0.50	12.1	11.9
0.24	0.24	6.0	6.3
0.18	0.18	5.5	5.2
0.48	0.25	8.0	14.1
0.25	0.45	14.5	8.4
X=Br, 61.5°			
0.51	0.49	~18.9	~19.2
0.28	0.27	6.6	6.7
0.22	0.17	4.8	4.8
0.54	0.24	8.5	16.1
0.24	0.54	11.7	6.4

The effects of concentration variation on the pre-exchange life-times for the CH_3HgI/CH_3HgCN, CH_3HgBr/CH_3HgCN, and CH_3HgCl/CH_3HgCN systems in DMF (Table 3) support a second-order kinetic process which may proceed via a bimolecular mechanism, of the form:



$$\underset{(A)}{CH_3HgX} + \underset{(B^*)}{\overset{*}{C}H_3HgCN} \xrightarrow{k_3} \left[CH_3Hg\begin{smallmatrix}X\\ CN\end{smallmatrix}Hg\overset{*}{C}H_3\right] \rightarrow \underset{(A^*)}{\overset{*}{C}H_3HgX} + \underset{(B)}{CH_3HgCN} \qquad (2)$$

or, which might involve pre-exchange equilibria in which solvent-separated ion pairs are formed:

$$CH_3HgX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3Hg^+||X^- \qquad CH_3HgCN \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3Hg^+||CN^-$$

$$\underset{(B^*)}{\overset{*}{C}H_3Hg^+||CN^-} + \underset{(A)}{CH_3Hg^+||X^-} \xrightarrow{k_3} \underset{(A^*)}{\overset{*}{C}H_3Hg^+||X^-} + \underset{(B)}{CH_3Hg^+||CN^-} \qquad (3)$$

The first emphasizes the covalent nature of the transition state with the bridging ability of the halide, as opposed to pseudohalide, being an important factor in forming a stable transition state. The second emphasizes the importance of a pre-equilibrium ion-pair formation to give a reactive solvent-separated ion-pair[12,13]. A bimolecular rate-determining process should yield expressions for the inverse mean lifetimes of halide groups on the two sites as follows:

$$1/\tau_A = \frac{k_3}{2}\cdot[B] \qquad 1/\tau_B = \frac{k_3}{2}\cdot[A]$$

The order of decreasing rate of methylmercury halide exchange with methylmercury cyanide is Br > Cl > I, the order of reactivity observed for reaction of the halides with dimethylmercury in dioxane[6]. The results imply that among the halides, bromine forms the most stable four-center transition state, or most readily forms solvent-separated ion-pairs. In the process described by eqn. (3), the activation enthalpy contains the sum of the enthalpy changes in each of two equilibria proceeding reaction:

$$\text{rate} = \frac{k_3}{2}\cdot[CH_3Hg^+||CN^-]\cdot[CH_3Hg^+||X^-]$$

$$[CH_3Hg^+||CN^-] = (k_1/k_{-1})\cdot[CH_3HgCN] = K_1\cdot[CH_3HgCN]$$
$$[CH_3Hg||X^-] = (k_2/k_{-2})\cdot[CH_3HgX] = K_2\cdot[CH_3HgX]$$

$$\text{rate} = \frac{k_3}{2}\cdot K_1\cdot K_2\cdot[CH_3HgCN]\cdot[CH_3HgX]$$

$$\text{rate} = \frac{k_3}{2}\cdot e^{-\Delta S_1/R}\cdot e^{-\Delta H_1/RT}\cdot e^{-\Delta S_2/R}\cdot e^{-\Delta H_2/RT}\cdot[CH_3HgCN]\cdot[CH_3HgX]$$

It may be assumed that reaction of the solvent-separated ion pairs, eqn. (3), is diffusion-controlled, and proceeds with a low activation energy. Since the equilibrium involving CH_3HgCN is common to the systems, the observed variation in activation energy must be ascribed largely to variation in the enthalpy change in the equilibrium.

$$CH_3HgX \rightleftarrows CH_3Hg^+\|X^- \qquad (X^- = Cl^-, Br^-, I^-)$$

Halide exchange for the systems CH_3HgCl/CH_3HgI and CH_3HgBr/CH_3HgI is rapid even at −71° in DMF. This represents a factor of about 10^4 in the rate constant compared to those in Table 4. Unfortunately, precipitation of the solutes from solution at low temperatures prevents detailed kinetic studies. Presumably a bimolecular mechanism of the type described by either eqn. (2) or (3) is operative. A low energy exchange-process for a bimolecular pathway is not uncommon[14–16]. Hatton *et al.*[5] observed that exchange of methyl groups, via halide exchange, between the two magnetically distinct sites is rapid for the CH_3HgI/CH_3HgSCN and CH_3HgCl/CH_3HgSCN systems, but is slow for CH_3HgCN/CH_3HgSCN at room temperature in pyridine. This is another example of the strong influence of the nature of the bridging group in the transition state on the rate of exchange. After standing for several days the DMF solutions exhibit more rapid exchange than when freshly prepared. For example, the coalescence temperature observed in the proton spectrum of a CH_3HgI/CH_3HgCN sample was observed to decrease by about 30° when a stock solution was allowed to remain at room temperature for several days. This does not appear to arise from an extensive decomposition of the solute. A methylmercury iodide solution kept at 100° for several days in a sealed NMR tube showed no trace of decomposition products in the NMR spectrum.

A series of solutions was studied in which $HgBr_2$, HgI_2, tetramethylammonium bromide or tetramethylammonium iodide was added to CH_3HgI/CH_3HgCN solutions in DMF. Mercuric halides react with CH_3HgCN to form an equilibrium mixture of CH_3HgX, $HgX(CN)$, CH_3HgCN and $Hg(CN)_2$. Formation of CH_3HgX is favored, as the data in Table 4 show. For example, addition of 0.5 *M* $HgBr_2$ to a 0.5 *M* CH_3HgI/0.5 *M* CH_3HgCN solution results in two CH_3 resonance absorptions, one due to all the rapidly exchanging CH_3HgX species, the other due to CH_3HgCN. From the relative areas it can be deduced that the concentration of CH_3HgCN is only 0.1 *M*. Mercuric bromide also appears to react with CH_3HgI to give an approximately statistical distribution of CH_3HgBr and CH_3HgI, as estimated from the chemical shift of the exchange-averaged CH_3HgX absorption.

The rate of exchange is increased by addition of mercuric halide. It is evident from the $1/\tau$ values in Table 4 that HgI_2* has a greater effect than an equal concentration of $HgBr_2$.

Addition of $N(CH_3)_4Br$ or $N(CH_3)_4I$ to CH_3HgI/CH_3HgCN mixtures in DMF results in rapid partial disproportionation of CH_3HgI into $(CH_3)_2Hg$ and HgI_2 (Table 5). The spectra were not observed to be time-dependent, indicating that equilibrium is attained within a few hours at most. In the case of $N(CH_3)_4Br$ addition, the chemical shift of the exchange-averaged CH_3HgX resonance is intermediate

---

* The purification of CH_3HgI by recrystallization from ethanol after preparation from $(CH_3)_2Hg$ and HgI_2 was observed to give exchange rates with CH_3HgCN similar to those seen on addition of HgI_2 to the CH_3HgI/CH_3HgCN system in DMF. The effect is very probably due to catalysis by traces of mercury iodide in the recrystallized material. Ethanol itself was observed to have no catalytic effects on exchange in the CH_3HgCN/CH_3HgI system in DMF.

TABLE 4

CHEMICAL SHIFTS AND FINAL CONCENTRATIONS OF SOLUTIONS INITIALLY 0.5 *M* EACH IN CH_3HgI AND CH_3HgCN, AFTER ADDITION OF MERCURIC HALIDES, AT 45° IN DMF

Added	$\delta^a(CH_3HgX)$ (Hz)	$\delta^a(CH_3HgCN)$ (Hz)	$[CH_3HgX]$ (*M*)	$[CH_3HgCN]$ (*M*)	$1/\tau(CH_3HgX)$	$1/\tau(CH_3HgCN)$
None	104.3	132.5	0.5 (I)	0.5	1.7	1.8
0.1 *M* HgI_2	104.4	133.0	0.62 (I)	0.38	8.2	13.4
0.5 *M* HgI_2	103.1	131.3	0.77 (I)	0.22	6.0	7.9
0.1 *M* $HgBr_2$	105.0	132.3	0.65 (I, Br)	0.35	2.4	7.2
0.5 *M* $HgBr_2$	107.7	131.7	0.90 (I, Br)	0.10	3.6	4.7

[a] Chemical shifts are in Hz, upfield from the high field DMF methyl resonance; δ for CH_3HgI is 104.6 Hz, for CH_3HgBr is 109.6 Hz, for CH_3HgCN is 133.2, all ± 0.5 Hz.

TABLE 5

MOLAR CONCENTRATIONS OF SPECIES PRESENT AT EQUILIBRIUM BASED ON PROTON NMR SPECTRA AT 35° IN SATURATED SOLUTIONS OF $N(CH_3)_4Br$ AND $N(CH_3)_4I$ IN DMF SOLUTIONS INITIALLY 0.5 ± 0.1 *M* EACH IN CH_3HgI AND CH_3HgCN

Solute	$[CH_3HgX]$ (*M*)	$\delta(CH_3HgX)$ (Hz)	$[CH_3HgCN]$ (*M*)	$\delta(CH_3HgCN)$ (Hz)	$[(CH_3)_2Hg]$ (*M*)	$\delta[(CH_3)_2Hg]$ (Hz)
$N(CH_3)_4I$	0.3	103.4	0.5	132.8	0.2	162.1
$N(CH_3)_4Br$	0.3	107.2	0.6	129.9	0.2	159.3

between that for CH_3HgI and CH_3HgBr (Table 5); there is evidently some reaction of the salt with CH_3HgI to produce CH_3HgBr. It is not possible to assess the extent of the reaction quantitatively from the chemical shift, since the salts apparently produce changes in chemical shifts, as evidenced by the different values obtained for the CH_3HgCN and $(CH_3)_2Hg$ resonances in the two cases.

The exchange reaction is very much accelerated in the presence of the tetramethylammonium halides. The coalescence temperatures for DMF solutions initially 0.5 *M* each in CH_3HgI and CH_3HgCN drop from about +100° for freshly prepared solutions to +10° for solution saturated (< 0.1 *M*) with either $N(CH_3)_4Br$ or $N(CH_3)_4I$.

It seems likely that halide ion is responsible for the accelerations in rate. Free halide ion[17] and mecuric halides[18] have been observed before to be catalytic. Complex formation with CH_3HgX (where X could be I, Br or CN) to form CH_3HgXY^- (where Y could be I or Br), would lead to a facile exchange by any one of a number of possible pathways. There is not at present sufficient information available to justify a definitive statement regarding the intimate mechanism.

Exchanges in pyridine solutions

Despite numerous attempts, and the most painstaking care, quantitatively reproducible data for the exchanges in pyridine solutions could not be obtained. Nevertheless, a number of useful results were obtained.

There is apparently catalysis by one or more products of disproportionation or reaction with solvent. Freshly prepared solutions which exhibited the slowest exchange rates in pyridine, and thus were probably least affected by catalysis, were consistently found to have a coalescence temperature on the order of 0 to +10°. Thus, the exchanges are clearly much faster in pyridine than in DMF. Dilution studies were also hampered by the catalysis effects, but the overall pattern of results indicates that the uncatalyzed exchange is bimolecular. An approximate Arrhenius activation energy of 20 ± 5 kcal/mole was obtained for the CH_3HgI/CH_3HgCN system. The closeness of the activation energy in pyridine to that obtained for DMF solution (21 ± 2 kcal/mole) indicates that a substantial contribution to the large difference in $\Delta G^{\neq}$ for the two solvents must arise from a more positive value for the entropy of activation, $\Delta S^{\neq}$, for the pyridine solutions, to the extent of about 15 e.u.

It is reasonable that $\Delta S^{\neq}$ should be less negative for the bimolecular pathway in a more strongly solvating medium. The basic solvent coordinates to force a quasi-tetrahedral geometry at the metal atom. The solvated CH_3HgX moiety is thus in approximately the correct geometry for the transition state, in which the bridged intermediate is formed*.

The ordering of halide reactivities for exchange with methylmercury cyanide in pyridine is $Cl \gg Br \sim I$, a notable change in relative reactivities as compared with the DMF solutions.

The pyridine solutions differ markedly from the DMF solutions in that the methylmercury halides undergo extensive disproportionation, to form dimethylmercury and mercuric halide. At room temperature equilibrium is attained in about

---

* This model is also applicable to exchange of alkyl groups in dialkylcadmium which also exhibits a sensitivity to solvent basicity[19].

a week, with formation of approximately 20 mole percent $(CH_3)_2Hg$. Disproportionation might occur through formation of a complex of the form $[C_5H_5NHgCH_3]^+$-I^-, which then disproportionates to $(CH_3)_2Hg$ and HgI_2. Similar complexes and their disproportionations have been described by Coates and Lauder[21]. Mercuric halides, and possibly free halide ions, are thus present in the pyridine solutions. The rates of exchange for samples which have apparently reached equilibrium with respect to disproportionation are, however, only slightly increased over those for freshly prepared solutions kept frozen.

It is clear, therefore, that variation in exchange rates over a range of about tenfold for apparently undisproportionated, fresh samples in pyridine results from the presence of an intermediate, possibly the $[C_5H_5NHgCH_3]^+X^-$ species mentioned above.

Attempts to extend the observations to other solvents were blocked by solubility limitations. Among the solvents examined and rejected on these grounds are diethyleneglycol, dimethyl ether, tetrahydrofuran, ether, 1,2-dimethoxyethane, triethylamine, acetonitrile, carbon disulfide, dimethyl sulfide and hydrocarbons. It was possible to obtain at least some information on solvent effects, however, by adding various bases to DMF solutions 0.5 *M* each in CH_3HgI and CH_3HgCN. The solutions were made 2 *M* in added base, and the effect on the exchange rate, as evidenced by the coalescence temperature was noted. The coalescence temperatures for the following bases were: +10° for pyridine and triethylamine; +60° for acetonitrile, tetrahydrofuran, and dimethylsulfide; and +100° for DMF. Quantitative comparisons are not easily made, because of the possibility of extraneous catalytic effects associated with the presence of the bases.

ACKNOWLEDGEMENTS

This research was supported by a grant from the National Science Foundation, GP 6396X. The authors are indebted to Mr. W. G. McDugle, Jr. for helpful discussion and assistance.

REFERENCES

1 R. B. Simpson, *J. Chem. Phys.*, 46 (1967) 4775.
2 N. S. Ham, E. A. Jeffery, T. Mole and S. N. Stuart, *Chem. Commun.*, 6 (1967) 254.
3 D. N. Ford, P. R. Wells and P. C. Lauterbur, *Chem. Commun.*, 13 (1967) 616.
4 P. R. Wells, W. Kitching and R. S. Henzel, *Tetrahedron Lett.*, (1964) 1029.
5 J. V. Hatton, W. G. Schneider and W. Siebrand, *J. Chem. Phys.*, 39 (1963) 1330.
6 Marvin D. Rausch and John R. Van Wazer, *Inorg. Chem.*, 5 (1964) 761.
7 Larry M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, 88 (1966) 4140.
8 C. S. Johnston, Jr., *Advan. Magnetic Resonance*, 1 (1965).
9 Raymond E. Dessy and Y. K. Lee, *J. Amer. Chem Soc.*, 82 (1960) 689; R. E. Dessy, Y. K. Lee and Jim-Young Kim, *J. Amer. Chem. Soc.*, 83 (1961) 1163.
10 C. R. McCoy and A. L. Allred, *J. Amer. Chem. Soc.*, 84 (1962) 912; R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, Alan Chen and T. Chivers, *J. Amer. Chem. Soc.*, 88 (1966) 460.
11 Z. Rappaport, P. D. Sleezer, S. Winstein and W. G. Young, *Tetrahedron Lett.*, (1965) 3719.
12 J. Smid and T. E. Hogen-Esch, *J. Amer. Chem. Soc.*, 88 (1966) 307, 318.
13 K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 88 (1966) 4134.
14 J. P. Maher and D. T. Evans, *J. Chem. Soc.*, (1963) 5534.
15 K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 88 (1966) 5460.
16 J. B. DeRoos and J. P. Oliver, *J. Amer. Chem. Soc.*, 89 (1967) 3970.

17 Raymond E. Dessy and W. Kitching, *Advan. Organometal. Chem.*, 4 (1966) 267. and references therein.
18 M. M. Kreevoy, D. J. W. Goon and R. A. Kayser, *J. Amer. Chem. Soc.*, 88 (1966) 5529.
19 N. S. Ham, E. A. Jeffrey, T. Mole, J. K. Saunders and S. N. Stuart, *J. Organometal. Chem.*, 8 (1967) P7
20 R. E. Dessy, F. Kaplan, G. Coe and R. H. Salinger, *J. Amer. Chem. Soc.*, 85 (1963) 1191.
21 G. E. Coates and A. Lauder, *J. Chem. Soc.*, (1965) 1857.