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$$\ln \frac{[CH_3Hg^+] - [5]}{[CH_3Hg^+]} = k_{exp}\tau[\text{alkene}]$$

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Nuclear Magnetic Resonance Studies on Anion-Exchange Reactions of Alkylmercury Mercaptides[1]

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Abstract: NMR experiments aimed toward elucidation of the mechanism of anion exchange of alkyl mercurials is described. Mercaptide anion exchange in RHgSR′/RHgSR″ systems exhibits second-order kinetic behavior. Evidence is presented that anion exchange proceeds through a four-center bridged intermediate with total exclusion of an ionic pathway.

The importance of alkylmercury mercaptides (RHgSR′) as a class of compounds has become increasingly obvious with recent disclosures of widespread mercury contamination in the environment. Methylmercury derivatives[2a] have received particular attention, since these compounds are produced in living systems from a variety of organic and inorganic mercury species. The unusually strong covalent bond between mercury and sulfur has prompted the suggestion[2b] that alkylmercury derivatives are carried through complex biological systems containing the sulfhydryl group (ORG-SH) as mercaptides by the exchange process given in the equation

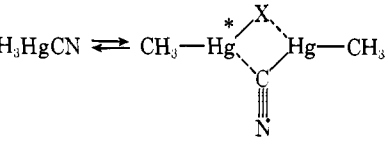
$$RHgSR' + ORG{-}SH \rightleftharpoons RHgS{-}ORG + R'SH \quad (1)$$

Indeed, the generic term mercaptan was coined because of the avidity of thiols for ionic mercury. The biosynthesis of methylmercury has, in fact, been shown to be stimulated in the presence of mercaptans.[3]

Despite the biological significance of sulfur as a ligand, spectral and structural studies on these organomercurials have only recently been carried out. The vibrational spectrum of CH_3HgSCH_3[4] and the infrared and mass spectral properties of C_6H_5HgSCN[5] have been reported. Spectral studies of the complexation of CH_3HgSCN with SCN^- have also been published.[6] Although a number of NMR studies on sulfur-containing mercurials have appeared,[7-13] a systematic NMR investigation of the mechanism of the exchange reaction of a methylmercury mercaptide with a sulfhydryl group has never been reported.

NMR studies have shown that rapid intermolecular-exchange reactions of methylmercury halides and pseudohalides proceed by a second-order pathway. The exchange has been established as proceeding by transfer of the ligand on mercury without carbon–mercury bond rupture.[7,14] A mechanism involving the four-center bridged transition state **1** was invoked for the CH_3HgCN/CH_3HgX exchange process (eq 2).

$$CH_3Hg^*X + CH_3HgCN \rightleftharpoons$$



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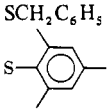
$$\rightleftharpoons CH_3HgX + CH_3Hg^*CN \quad (2)$$

However, a pre-exchange equilibrium in which solvent-separated ion pairs were formed could not be excluded.

The controversy concerning an ionic mechanism versus a pathway utilizing covalently bound species forming a bridged transition state in mercury-exchange reactions had its origin in a series of papers by Hughes, Ingold, and co-workers.[15] They stated that one alkyl mercury exchange of RHgX with $^*HgBr_2$ could not be explained on the basis of a "closed" or bridged transition state. More recently, arguments that the proposed alkyl group exchange via an "open transition state" violates the principle of microscopic reversibility have been presented.[16] This criticism, however, has since been challenged.[17] Thus, the mechanism for alkyl and anion exchange in RHgX compounds still remains in question.

In the present study, we report a series of NMR experiments aimed toward elucidation of the mechanism of anion exchange of alkyl mercurials. Our data provide the first unequivocal evidence for anion exchange involving a four-center bridged intermediate in the exchange of an alkyl mercury mercaptide with the total exclusion of an ionic mechanism. We have also developed a model system that has provided fundamental information concerning viable pathways for methylmercury migration in biological systems.

Table I. NMR Parameters and Stability Constants for MeHgX Derivatives

Compd	X	δ CH_3Hg[a] in CH_2Cl_2	$^2J(^{199}Hg-^1H)$[a] in CH_2Cl_2	log K_{stab} (lit. values)	log K_{stab} (calcd)[b]
2a	$OC(=O)CH_3$	1.04	212.2	3.6[d]	3.3
2b	Cl	1.09	205.2	5.25[e]	4.9
2c	SCN	1.21 (0.94)[c]	192.0 (212.0)	6.05[e]	8.0
2d	Br	1.15	199.6	6.62[e]	6.2
2e	CN	0.88 (0.58)	171.4 (179.3)	14.1[e]	12.8
2f	$SC(=O)CH_3$	0.76	167.4		13.8
2g	$SCH_2C(=O)OCH_3$	0.83	164.0		14.5
2h	SC_6H_4Cl-*p*	0.92 (0.80)	161.7 (171.3)		15.1
2i	SC_6H_5	0.89 (0.79)	161.5 (168.4)	14.67[f]	15.1
2j	$SC(C_6H_5)_3$	0.41	159.8		15.5
2k	SCH_3	0.82 (0.66)	157.1 (158.2)		16.2
21	$SHgCH_3$	0.77	156.6	16.3[e]	16.3
2m	$SCH_2C_6H_5$	0.57	156.6		16.3
2n		0.77	156.0		16.4
2p	$SC(CH_3)_3$	0.77	150.2		17.8

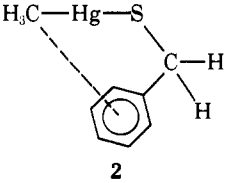
[a] NMR parameters were obtained on 0.05–0.1 M CH_2Cl_2 solutions. δ is the proton chemical shift in parts per million downfield from Me_4Si. *J* values are in hertz. [b] The relationship that log $K_{stab} = 52.85 - 0.2336J$ was established by the linear least-squares analysis of the plot of previously determined log K_{stab} values vs. $^2J(^{199}Hg-^1H)$ values determined in this study for CH_2Cl_2 solutions of CH_3HgX. The error limits were 3.77 for the intercept and 0.02 for the slope. [c] Values in parentheses were measured in DMF. [d] Reference 7b. [e] Reference 9. [f] Cited in ref 10a.

Results and Discussion

In CH_3HgX compounds, spin coupling between the ^{199}Hg nucleus (abundance 16.86%) and the protons of the methyl group provides a doublet symmetrically situated about the central methyl resonance. This coupling interaction has been attributed[18] to a Fermi contact interaction, wherein the magnitude of the coupling constant $^2J(^{199}Hg-^1H)$ increases with increasing contribution of the mercury 6s orbital to the C–Hg bond. In prior studies, analysis of $J(^{199}Hg-CH_3)$ spin-coupling constants in the NMR spectra of a wide variety of CH_3HgX substrates has afforded a linear relationship with the logarithm of the stability constants for CH_3HgX formation,[10b] the p*K*'s of the monobasic parent acids HX,[11b,12] and the chemical shifts of the methyl group.[8] The stability constants for seven CH_3HgX derivatives have been measured[7b,9] in aqueous solution (Table I). Thus, a measure of the relative magnitude of these coupling constants for the alkylmercury mercaptides should provide a means of probing the strength of the mercury–sulfur bond. These data are vital to our mechanistic study, since we need to be able to estimate the $[CH_3Hg^+]$ and $[X^-]$ in solution. As anticipated, a plot of the log $[CH_3HgX]/[CH_3Hg^+][X^-]$ vs. the values of $^2J(^{199}Hg-^1H)$ obtained in CH_2Cl_2 solvent afforded a linear relationship (correlation coefficient = 0.98) with a slope of −0.2336 and an intercept of 52.85. We have estimated the extent of ionization of the series of CH_3HgX derivatives given in Table I by using the relationship: log $K_{stab} = 52.85 - (0.2336\ ^2J(^{199}Hg-^1H))$. With the possible exception of CH_3HgCN and CH_3HgSCN, there is good agreement between experimental and calculated stability constants. The calculated K_{stab} for CH_3HgSCH_3 also agrees well with the reported[9] K_{stab} (16.12) for $CH_3HgSCH_2CH_2OH$. In addition, the stability constants for the methylmercury derivatives of cysteine (15.7) and histidine (15.9)[7b] are of the same magnitude as our calculated values in general.

This is a gratifying correlation, since the stability constants were measured in water while the coupling constants were taken in methylene chloride. Since the methyl mercurials are not highly dissociated in a nonpolar solvent, the calculated K_{stab} probably reflect an upper limit. This type of behavior was first pointed out by Scheffold, who reported a linear correlation between coupling constants of CH_3HgX derivatives measured in water and in pyridine solvent.[10]

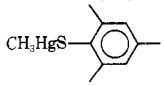
The increased bond order of the Hg–S bond should be occasioned by an increase in sp hybridization of mercury, resulting in a decrease in the $J(^{199}Hg-^1H)$ coupling constant attendant upon a decrease in s character in the C–Hg bond. Based on extended Hückel calculations,[18] the percent 6s character in the C–Hg bond of CH_3Hg^+, CH_3HgF, CH_3HgCl, CH_3HgSH, and CH_3HgCH_3 is 92.0, 70.1, 65.2, 61.4, and 57.6% respectively. Consistent with these data, the mercury–proton coupling constants range from 233.2 Hz for CH_3HgClO_4, which is essentially completely ionized, to 104.3 Hz for the highly covalent dimethylmercury. The thermodynamic stability of the series of methylmercury mercaptides studied also appears to directly parallel the electron density at sulfur. The calculated K_{stab} values are consistent with intuitive expectations for the extent of ionization of CH_3HgSR based upon the electron withdrawing tendency of the substituent on sulfur (i.e., R = $C(=O)CH_3 > C_6H_5 > CH_3 > C(CH_3)_3$). However, the proton chemical shifts of the methyl groups for the majority of the CH_3HgSR compounds studied are centered at δ 0.82 ± 0.1 and are not markedly influenced by the R group. Similarly, the stretching frequency of the carbon–mercury bond for this series of methylmercury compounds containing a variety of ligands is not responsive to the apparent electronegativity of the ligand or to the hybridization of the mercury (Table II). However, when R = $\geqslant CC_6H_5$ the methyl protons experience an upfield shift which is presumably due to the anisotropy of the aromatic ring of the benzyl group. The methyl group in **2** was estimated to be ~4.6 Å above the



2

center of the ring. Based upon published values[19] for aromatic ring current anisotropy effects this should give rise to an upfield shift of 0.32–0.47 ppm, depending upon the position of the methyl group above the ring. The methyl proton resonance for $CH_3HgSCH_2C_6H_5$ occurs at 0.4 ppm above that of CH_3HgSCH_3 in CH_2Cl_2, in excellent agreement with this prediction. NMR and preliminary x-ray data[20] for 3-aryl-

Table II. Infrared Data on Methylmercury Derivatives[a]

Compd	ν_{Hg-C}	Ref
CH_3HgCH_3	540 (neat)	*b*
	538	*c*
CH_3HgCl	558 (CH_2Cl_2)	
	557 (benzene)	
	552	*c*
CH_3HgI	535 (benzene)	
	531	*c*
CH_3HgSCH_3	539 (benzene)	
	534 (neat)	
	533 (neat)	*d*
$CH_3HgSCH_2C_6H_5$	535 (neat)	
$CH_3HgSC_6H_5$	540 (benzene)	
	542 (CH_2Cl_2)	
$CH_3HgSC_6H_4$-Cl-*p*	543 (benzene)	
	537 (benzene)	
$[(CH_3Hg)_3S]NO_3$	535	*c*

[a] All spectra reported in our work were recorded on a Perkin-Elmer 521 grating spectrophotometer using polyethylene cells and indene as a calibrating standard. [b] J. L. Bribes and R. Gaufres, *J. Chim Phys.*, 67, 1168 (1970). [c] J. H. S. Green, *Spectrochim. Acta, Part A*, 24, 863 (1968). [d] Reference 4.

propylmercury derivatives have suggested an intramolecular mercury–aromatic ring interaction with the mercury atom located 3.05 Å above the edge of the benzene ring. The crystal structure[21] of $C_6H_5CH_2HgSC(C_6H_5)_3$ also suggests a Hg–C_6H_5 interaction at a distance of 3.3 Å.

With the apparent exception of CH_3HgSR compounds, the affinity of the ligand X for CH_3Hg^+ affects both the chemical shift of the methyl group and the magnitude of the mercury–proton coupling constants. In all of the above cases, the observation of this spin coupling precludes rapid carbon-mercury bond cleavage since this would give rise to a single methyl resonance in a magnetic environment averaged over all mercury spin states.[7a] The NMR spectra of the individual alkylmercury mercaptides (**2f–p**) and binary mixtures of these compounds in CH_2Cl_2 solvent all exhibited ^{199}Hg–^1H coupling suggesting that the CH_3–Hg bond is not labile under these conditions.

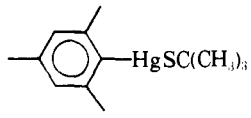
In view of the thermodynamic stability of these mercaptides, long-range mercury–proton coupling through the sulfur bond was an intriguing possibility. Mercury–proton coupling through four bonds in $(CH_3)_3CCH_2HgX$[22a] and across the ring to the para methyl group in *p*-$CH_3C_6H_4HgX$[22b] has been observed. In addition, $^3J(^{199}Hg$–$^{19}F)$ coupling in $Hg(SCF_3)_2$[23a] and $^4J(^{199}Hg$–$^{19}F)$ coupling in $CF_3C_6H_4HgX$ derivatives have been observed.[23b] Proton–proton coupling in $HSC(CH_3)_3$, $^4J(H$–$H) = 0.5$ Hz, is also clearly discernable. However, in no case could $J(^{199}Hg$–S–CH) coupling be observed in the present study in CH_2Cl_2 solvent at temperatures ranging from 38 to −70 °C. The failure to observe mercury coupling associated with the –SR moiety strongly suggested that rapid exchange of the mercaptide ligands was occurring. Consistent with this suggestion, binary mixtures of equal amounts of CH_3HgSR and CH_3HgSR' showed a single resonance for the methyl group at a chemical shift which was an average of the chemical shifts of the individual compounds.

In an effort to slow down mercaptide anion exchange we prepared several sterically hindered alkylmercury mercaptides. For a given system the exchange rate should be subject to both steric and dipole interactions. The NMR spectrum of $(CH_3)_3CHgSC(CH_3)_3$ (**4c**) (0.1 M) in CH_2Cl_2 at −70 °C consisted of two intense lines, only one of which was associated with satellites (Table III). Similarly, no evidence for long-range mercury–proton coupling could be observed with the highly

Table III. NMR Data on $(CH_3)_3CHgX$ Derivatives[a]

Compd	X	δ $C(CH_3)_3$	$^3J(^{199}Hg$–$^1H)$
4a	–Cl	1.58	256.4
4b	$-SCH_3$	1.41	183.0
4c	$-SC(CH_3)_3$	1.46	180.8
4d	$-SCH_2C_6H_5$	1.22	188.4
4e	$-SC_6H_4NO_2$-*p*	1.50	212.2
4f	$-SCH(CH_3)C_6H_5$	1.18	189.8

[a] NMR parameters were obtained on 0.05–0.1 M CH_2Cl_2 solutions at 38 °C. The proton chemical shift (δ) is reported in parts per million downfield from Me_4Si. *J* values are given in hertz.



hindered mesityl derivative (**5**). Rapid anion exchange was confirmed by examining the NMR spectrum of a binary mixture of **4c** and **5** in CH_2Cl_2 at −60 °C. Although the individual resonances for the $-SC(CH_3)_3$ protons are separated by 4.8 Hz, only one absorption due to protons was observed at an intermediate frequency.

Having established that anion exchange in alkylmercury mercaptides is unusually fast, we turned our attention to the elucidation of a general mechanism for these reactions. Five mechanisms for this rapid anion or potential anion exchange may be considered: (1) bimolecular anionic attack of Y^- on CH_3HgX which may either proceed by direct nucleophilic displacement or by formation of a complex ion intermediate (eq 3); (2) a bimolecular ionic mechanism proceeding by electrophilic attack of CH_3Hg^+ on CH_3HgY (eq 4); (3) pre-exchange ion-pair formation to give a reactive solvent-separated ion pair (eq 5); (4) exchange involving two reactive solvent-separated ion pairs (eq 6); (5) a bimolecular exchange involving the four-center intermediate **6** in the absence of ion formation (eq 7).

$$RHgX + Y^- \rightleftharpoons R-\overset{-}{Hg}\begin{matrix}X\\Y\end{matrix} \rightleftharpoons RHgY + X^- \quad (3)$$

$$CH_3\overset{*}{Hg}^+ + CH_3HgY \rightleftharpoons CH_3\overset{*}{Hg}Y + CH_3Hg^+ \quad (4)$$

$$CH_3\overset{*+}{Hg}\|X^- + CH_3HgY \rightleftharpoons CH_3\overset{*}{Hg}X + CH_3\overset{+}{Hg}\|Y^- \quad (5)$$

$$CH_3\overset{*+}{Hg}\|X^- + CH_3Hg\|Y^- \rightleftharpoons CH_3\overset{*+}{Hg}\|Y^- + CH_3\overset{+}{Hg}\|X^- \quad (6)$$

$$CH_3\overset{*}{Hg}X + CH_3HgY \rightleftharpoons \left[CH_3-\overset{*}{Hg}\begin{matrix}X\\Y\end{matrix}Hg-CH_3\right]$$

6

$$\rightleftharpoons CH_3\overset{*}{Hg}Y + CH_3HgX \quad (7)$$

Kinetic evidence[7a] based upon an NMR study in aqueous medium of the exchange reaction of CH_3HgCN with OH^- supports a bimolecular anionic mechanism at pH greater than 10.3 (eq 3). A second mechanism was operating at pH below 9 and by the process of eliminating other mechanisms the exchange was attributed to a "direct" exchange, as suggested by eq 7. The involvement of methyl mercuric ion (eq 4) was ruled unlikely. A mechanism involving the bridged intermediate **1** was also preferred for CH_3HgCN/CH_3HgX (X = Cl, Br, I) anion exchange in DMF solvent.[2] One of the basic difficulties in excluding an ionic mechanism in the anion exchange is the plausible ionization of RHgX and a rapid diffusion-controlled exchange involving ions (eq 3 and 4) or reactive solvent-sep-

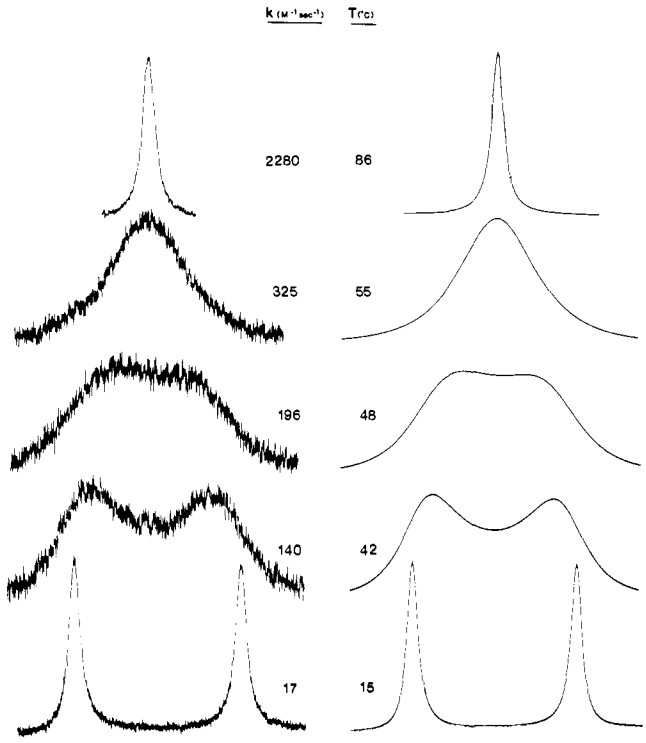


Figure 1. Theoretical and experimental spectra for exchange of $MeHgSC_6H_5/MeHgCN$.

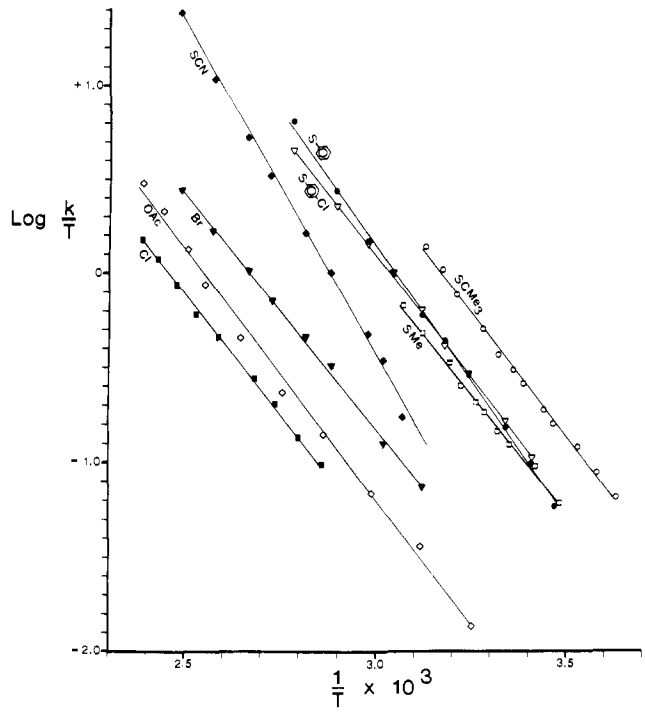


Figure 2. Activation parameter plots for MeHgX/MeHgCN exchange.

arated ion pairs (eq 5 and 6). These mechanisms are not distinguishable on the basis of kinetic data, since they should all exhibit second-order behavior. If an ionic mechanism were involved, the rate of exchange should be greater for the more highly dissociated mercurials. On the other hand, exchange involving the 4-center intermediate **6** should be facilitated by polarizable ligands that readily form bridged species. Structurally, the analogous RZnSR′ and RCdSR′ compounds have been shown to exist as tetramers or polymers depending upon the substituents.[24] The ionization of the Hg–X bond has been shown to increase in the order $RS^- < CN^- < BR^- < SCN^- < Cl^- < OAc^-$. The experimentally derived and calculated association constants for CH_3HgX formation from CH_3Hg^+ and the anions in Table I vary over 14 orders of magnitude. Thus, the trend observed for the rates of anion exchange in this series should provide a definitive distinction in favor of an "open" or a "closed"[15] exchange pathway.

Our initial mechanistic probe was designed to examine the effect of the degree of dissociation of CH_3HgX on its anion exchange rate with CH_3HgCN (eq 2). By keeping the CH_3HgCN common to each exchange study, the variation in $\Delta G^{\ddagger}$ should be attributable largely to an enthalpy change if an ionic mechanism obtains or if extensive Hg–X bond breaking is involved in the rate-limiting step. Such an eventuality could conceivably arise if the mechanisms in eq 3–6 were operable. The observation of an extremely rapid anion exchange with the highly covalent CH_3HgSR derivatives would preclude an ionic mechanism, since the effective concentrations of CH_3Hg^+ or RS^- in solution would be prohibitively low.

The rates of anion exchange in the CH_3HgX/CH_3HgCN system in DMF solvent were determined by the complete line-shape analysis NMR method.[25] Second-order kinetic behavior for mercaptide anion exchange was demonstrated for the $CH_3HgSC_6H_5/CH_3HgCN$ system. The rapid exchange of methyl groups between magnetically distinct sites in CH_3HgX/CH_3HgCN(X = Cl, Br, I) in DMF solvent is also second order.[14] A comparison between experimental and theoretical spectra for this exchange process is given in Figure 1. The temperature dependance of the second-order rate constants so obtained was analyzed using an Erying ($\ln[k/T]$ vs. $1/T$) linear least-squares correlation (Figure 2). The thermodynamic parameters for these exchange processes are summarized in Table IV.

It is immediately obvious from our data that the rate of anion exchange increases with *increasing* K_{stab} of CH_3HgX. The trend noted for the $\Delta G^{\ddagger}$ for exchange is particularly illuminating, since this is the opposite trend to that anticipated if an ionic mechanism were operating. Thus, the methylmercury mercaptides, which are thermodynamically the most stable CH_3HgX substrates, are kinetically the most labile of the compounds studied. These results provide compelling evidence that none of the above ionic mechanisms (eq 3–6) are involved in mercaptide anion exchange with CH_3HgCN. This conclusion is based on the following arguments. The exchange of ligands involving two solvent-separated ion pairs (eq 6) should exhibit kinetic behavior consistent with the rate expression, rate = $k_2K_1K_3[CH_3HgX][CH_3HgCN]$, where K_1 and K_3 are equilibrium constants for substrate dissociation. If the equilibrium constants for ionization of either of the substrates are of the order of 10^{-3}–10^{-17}, then the observed rate of exchange is orders of magnitude too fast. Similarly, if only one ion pair is involved (rate = $(k_2/2)K_1[CH_3HgX][CH_3HgCN]$) the observed rate is too fast even if a diffusion-controlled anion exchange with $k_2 = 10^9$–10^{11} were assumed. However, the ionic mechanisms in eq 3 and 4 are not as readily excluded with the more ionic substrates **2a–d** (Table IV). For example, exchange proceeding by electrophilic attack of CH_3Hg^+ on CH_3HgCN, where the rate = $(k_2/2)(K_1[CH_3HgX])^{1/2}[CH_3HgCN]$ (assuming $[CH_3Hg^+] = [X^-]$), must be considered. Likewise, it is possible that the CH_3HgOAc/CH_3HgCN exchange could proceed by an ionic mechanism (eq 3) as suggested by Simpson[7a] for the CH_3HgCN/OH^- exchange. Nevertheless the overall consistency of the observed trend of $\Delta G^{\ddagger}$ provides a convincing argument that all of the above reactions, with the possible exception of CH_3HgOAc, undergo anion exchange through the intermediacy of a bridged species such as **1.**

The above conclusion that a bridged intermediate or transition state lies on the reaction pathway for anion exchange is

Table IV. Activation Parameters for the Exchange of CH_3HgX in DMF

Compd	X	[Me-HgX][a]	[Me-HgCN]	Temp range of study, °C	$\Delta\nu$[b]	T coal., °C (k_2)[c]	k_2[c] (25°C)	E_a[d]	$\Delta H^{\ddagger}$[e]	$\Delta S^{\ddagger}$,eu	$\Delta G^{\ddagger}$[e] (25 °C)	$\Delta G^{\ddagger}_{coal}$[f]
2b	Cl	0.27	0.25	77–146	18.9	128 (351)	1.5	12.5	11.6 ± 0.2	−18 ± 1	17.1	19.07 (19.10)
2a	OAc	0.276	0.284	35–145	15.4	114 (315)	2.2	12.9	12.1 ± 0.3	−16 ± 1	16.9	18.46 (18.67)
2d	Br	0.246	0.25	48–129	23.5	102 (383)	5.8	12.1	11.3 ± 0.2	−17 ± 1	16.3	17.72 (17.65)
2c	SCN	0.20	0.25	53–128	21.2	80 (506)	6.1	16.9	16.1 ± 0.3	− 1 ± 1	16.3	16.44 (16.65)
2k	SCH_3	0.27	0.25	14–53	4.0	34 (67)	38.0	11.9	11.2 ± 0.2	−13 ± 1	15.2	15.45 (15.41)
2i	SC_6H_5	0.254	0.246	15–86	12.1	49 (223)	40.0	13.8	13.0 ± 0.2	− 7 ± 1	15.2	15.46 (15.48)
2h	SC_6H_4Cl-*p*	0.264	0.25	20–86	12.6	47 (189)	45.0	12.5	11.7 ± 0.2	−11 ± 1	15.1	15.47 (15.36)
2p	$SC(CH_3)_3$	0.255	0.243	2–46	6.4	28 (120)	98.0	12.5	11.8 ± 0.3	− 9 ± 1	14.6	14.79 (14.81)

[a] Concentration in moles/liter. [b] Chemical shift difference in hertz of the methyl resonances at the coalescence temperature. [c] Second-order rate constant k (M^{-1} s^{-1}) were obtained by extrapolation of a least-squares plot of data obtained at at least eight other temperatures. Correlation coefficients of >0.9977 were obtained for each plot. The rate constants were calculated assuming a bimolecular mechanism where rate = $(k_2/2)[CH_3HgX][CH_3HgCN]$ and the observed rate of exchange $1/\tau_{CH_3HgX} = (k_2/2)[CH_3HgCN]$. [d] E_a was obtained by least-squares analysis of the Arrhenius plot of log rate vs. reciprocal absolute temperature. [e] $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ are given in kcal/mole; the error limits given are those derived from linear least-squares analysis of the Eyring plot of rate–temperature data. [f] The $\Delta G^{\ddagger}$ was determined using the complete line-shape analysis method. The values in parentheses were determined by the approximate equation $k_c = (\pi/\sqrt{2})(\Delta\nu)$.

buttressed by the fact that the relative exchange rates reflect the bridging propensity of the potential anion X. Thus, **2a** exhibited a slow exchange rate where presumably an oxygen bridge was involved. In contrast, the tendency for mercaptide sulfur to form three bonds and bridge metal atoms forming oligomeric compounds is well established.[26] Within the mercaptide series, the exchange rate appears to be facilitated by an increase in electron density at sulfur. This point is dramatically exemplified by the fact that the *tert*-butyl mercaptide **2p** exchanges faster than the methyl mercaptide **2k** despite the steric bulk of the *tert*-butyl group. It is also of interest to point out that a corollary of the aforementioned relationship between increased exchange rates and K_{stab} is an inverse relationship between the rates of exchange and the magnitude of the $^2J(^{199}Hg-^1H)$ coupling constant. All three variables appear to respond in a predictable manner to the inductive effects of the substituent on sulfur.

The activation parameters for the CH_3HgX/CH_3HgCN exchange studies (Table III) also lend credence to the suggestion that a bridged transition state (eq 7) is involved. There does not appear to be any correlation between the $\Delta H^{\ddagger}$ or E_a and K_{stab}. Although this observation supports the contention outlined above concerning enthalpic dominance in an ionic mechanism, this conclusion should be tempered by the fact that the $\Delta G^{\ddagger}$ obtained by the NMR method is often more reliable than $\Delta H^{\ddagger}$ (vide infra). Despite the fact that the entropies of activation may not be highly accurate, they are consistently negative, suggesting a considerable ordering of the transition state relative to the ground state. If, indeed, bridged transition states or structures comparable to **6** are involved in all of the above exchange reactions, then the differences in $\Delta S^{\ddagger}$ may reflect differences in solvent reorganization. Consistent with this suggestion is the observation that exchange with the more ionic substrates resulted in a more negative $\Delta S^{\ddagger}$, where more charge separation would be anticipated.

Another facet of the present study was to compare the general reliability of the use of approximate equations ($k_c = (\pi/\sqrt{2})(\Delta\nu)$) to the complete line-shape analysis method for this type of exchange reaction. Although the use of approximate equations has been criticized in the past as being unreliable, we found remarkable agreement between the $\Delta G^{\ddagger}_{coal}$ values obtained by the two methods (Table IV, footnote *f*) for the entire series of CH_3HgX/CH_3HgCN exchange reactions. Our interest in this aspect of our study was intensified by the recent systematic comparisons of the two methods by Kost[27a] and Raban.[27b] Both authors advocate the general validity of the approximate equations in most cases. Although we initiated our complete line-shape analysis studies with the view toward obtaining more quantitative data, we would have arrived at essentially the same conclusions using the approximate equations. However, if one wishes to also determine the activation parameters by conducting rate–temperature studies (Table V), then a line-shape analysis is recommended. Our experience in the present work also prompts us to emphasize that $\Delta G^{\ddagger}$ is a more reliable parameter than E_a for the comparison of related types of exchange processes. For example, our free energies of activation are in reasonable agreement with those we have calculated using data reported by Brown.[14] Using line-broadening techniques ($1/\tau_A = \pi(\Delta - \Delta^0)$) he determined a $\Delta G^{\ddagger}_{coal}$ = 19.8 kcal/mol for CH_3HgCl/CH_3HgCN exchange and $\Delta G^{\ddagger}_{coal}$ = 16.4 kcal/mol for CH_3HgBr/CH_3HgCN anion exchange. However, their reported E_a of 15 ± 2 and 9 ± 1 kcal/mol for these two processes in DMF are in poor agreement with those given in Table III. This discrepancy may possibly reflect the inability of the NMR technique to accurately separate the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms. As advocated above, we have based most of the conclusions in this study on the $\Delta G^{\ddagger}$ values measured.

Table V. Second-Order Rate Constants from Concentration-Variation Rate Data for $CH_3HgSC_6H_5/CH_3HgCN$ Exchanges in DMF

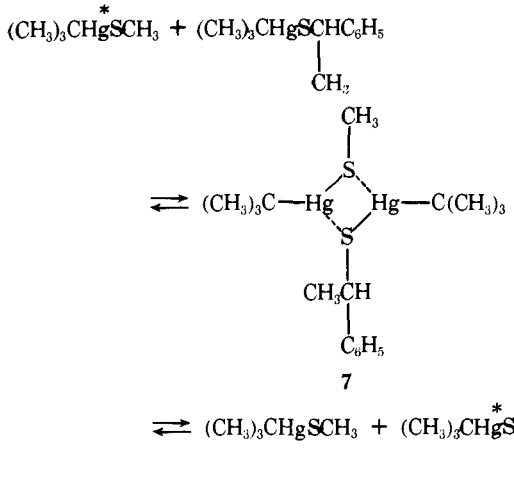
Concn of $CH_3HgSC_6H_5$, M	Concn of CH_3HgCN, M	T, °C 23.9	18.9	13.4
0.550	0.250	140	84	59
0.485	0.315	70	51	36
0.280	0.52	70	45	28
0.400	0.400	84	57	38

The significance of bridging in the transition state for CH_3HgX/CH_3HgCN anion exchange strongly suggested that an exchange reaction involving two mercaptide anions should proceed at an unprecedented rate. Our expectations were realized in a series of preliminary experiments when we discovered RHgSR′/RHgSR″ mercaptide anion exchange to be extremely facile. Our initial efforts to obtain reliable quantitative data were thwarted by the low solubility and line broadening associated with alkylmercury mercaptides at the low temperatures required to slow intermolecular exchange. We found that substituting a *tert*-butyl group for a methyl group not only allowed us to conduct our NMR measurements at lower concentrations but also afforded increased solubility. The necessary separation of the *tert*-butyl resonances under nonexchange conditions was fortuitously achieved by using a benzyl mercaptide, which exhibits the aromatic ring-current anisotropy discussed above (Table VI). Using the mixed sol-

Table VI. Concentration-Variation Rate Data for Mercaptide–Mercaptide Exchange

Run	$(CH_3)_3$-CHgSCH$_3$, M	$(CH_3)_3$-CHgSCH-(CH_3)-C_6H_5, M	$\frac{1}{\tau}$	k_2 (−135 °C)
1	0.0187	0.0204	129	12 640
2	0.0136	0.0136	67.4	9 920
3	0.0077	0.0074	32.9	8 960
4	0.0106	0.0115	60.7	10 600
5	0.0128	0.0044	25	10 880
6	0.0069	0.0104	43	8 120

vents $HCF_2Cl/HCFCl_2$ in a 4:1 ratio we measured the rate of mercaptide exchange for $(CH_3)_3CHgSCH_3/(CH_3)_3CHgSCH_2C_6H_5$ at temperatures down to −160 °C. Using the complete line-shape NMR method we determined that $\Delta G^{\ddagger} \simeq 5.4$ kcal/mol at −138 °C. An Erying plot of the rate-temperature data extrapolated to 25 °C afforded $\Delta G^{\ddagger}_{25°C} \simeq 8.0$ kcal/mol and $\Delta S^{\ddagger} = -16$ eu. Improved solubility and a greater separation of the *tert*-butyl resonances (13.5–14.5 Hz) was achieved by using α-methylbenzyl mercaptide. Although signal broadening still remains a problem, the *tert*-butyl lines coalesced at −142 °C with $(CH_3)_3CHgSCH_3/(CH_3)_3CHgSCH(CH_3)C_6H_5$ in the 4:1 $HCF_2Cl/HCFCl_2$ solvent system. The free energy of activation was found to be only 5.2 kcal/mol at −138 °C. Extrapolation of the data obtained at low temperature at seven different ratios of substrate to 25 °C gave $\Delta G^{\ddagger}_{25} = 7.3$ kcal/mol and $\Delta S^{\ddagger} = -12.7$ eu. The negative sign of entropy of activation is consistent with a bimolecular four-center transition state. The second-order kinetic behavior was confirmed by concentration-variation experiments and extrapolation of the data to 25 °C afforded the remarkable value for the rate constant of $k_2 = 3 \times 10^7$ s^{-1}M^{-1}. Since the equilibrium constant for ionization of a typical alkylmercury mercaptide is $\sim 10^{-16}$ in a polar solvent, any calculated exchange rates based upon the aforementioned ionic processes (eq 3–6) for the relatively nonpolar solvent system employed herein would be at least 10^5 greater than that of a mechanism involving preequilibrium ionization and diffusion-controlled anion exchange. These data thus provide the first unequivocal example of a bimolecular anion exchange of an alkylmercury compound (eq 8) with the



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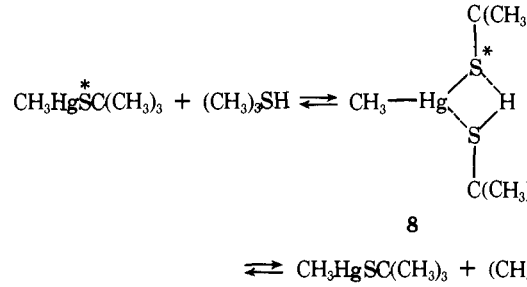
(8)

total exclusion of an ionic mechanism. These data further provide another viable pathway for alkylmercury migration in biological systems in addition to the more generally accepted exchange reaction with a sulfhydryl group (eq 1).

Having satisfied our initial objectives concerning the mechanism for anion exchange, we turned our attention to the mercaptan–mercaptide exchange reaction (eq 1). Our NMR studies have shown that bridging of the ligand between two metal atoms plays a significant role in lowering the $\Delta G^{\ddagger}$ for exchange. The loss of such bridging in the mercaptan–mercaptide exchange could in fact relegate this process to be considerably less facile than mercaptide–mercaptide exchange. Moreover, it was entirely conceivable that another mechanism, namely the anionic process in eq 3, could become dominant because of the nucleophilicity of RSH or its anion. When this exchange reaction (eq 9) was attempted in *o*-dichlorobenzene solvent, separate *tert*-butyl resonances for the mercaptan (0.02 M) and the mercaptide (0.041 M) were discernable at temperatures as high as 158 °C. Since the solvent polarity of *o*-dichlorobenzene does not differ significantly from the $HCF_2Cl/HCFCl_2$ mixed solvent used in mercaptide–mercaptide exchange, the marked difference in exchange rates buttresses the concept of exalted mercury–sulfur bridging in these exchange processes. The failure to observe rapid aryl mercaptan/arylmercury mercaptide exchange on the NMR time scale in chlorobenzene solvent has also been reported recently.[13] However, exchange was noted in the more basic solvent pyridine. We also observed mercaptide anion exchange (eq 9) in the more polar solvent DMF. Although a limited



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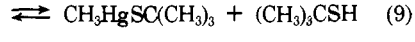

(9)

separation of the *tert*-butyl resonances limited the accuracy of our rate measurements, the $\Delta G^{\ddagger}_{25°C}$ for a 0.14 M solution of **2p** and 0.17 M *tert*-butyl mercaptan was estimated to be 16 kcal/mol. In other preliminary experiments, we have found the mercaptan–mercaptide exchange to be markedly accelerated by base. It would thus seem that the effective bridging of the hydrogen atom in transition state **8** is considerably less than that in **7**. Moreover, the catalytic effects of base strongly suggests that an anionic mechanism is operating. We will report more definitive details of the effects of solvent polarity and pH on the exchange mechanism in future papers.

One final objective of the present work was to further examine the interesting point raised by Dehnicke[5] concerning the possible dimeric structure of C_6H_5HgSCN in its crystalline state. Although he suggested that C_6H_5HgSCN was monomeric in camphor solution at 178 °C, he also reported infrared data consistent with a dimeric structure. In addition, the mass spectrum also evidenced ions of high mass such as $(C_6H_5)_2HgS^+$ and $C_6H_5(HgSCN)_2^+$, indicative of a dimeric structure. However, no relative intensities for these ions were given.

For all the compounds studied, the parent ion was clearly observable, providing a convenient method for proof of molecular composition.[28] The parent ions were more abundant for arylmercury compounds than they were for alkylmercury. In no case could we observe an ion with twice the mass of the parent ion, although low intensity fragments for $R_2Hg_2X^+$ and $R_2Hg_2S^+$ were observed. However, the relative intensities of these ions for C_6H_5HgSCN were comparable to those of CH_3HgSCH_3 and CH_3HgCN. Both of these compounds have been assigned a monomeric structure; the former on the basis of infrared and Raman spectroscopy[4] and the latter on x-ray data.[29] The assignment of a dimeric structure for these mercaptides on the basis of mass spectral data is therefore ques-

tionable. Additional evidence to support a monomeric structure is the recent x-ray structural determination[21] of $C_6H_5CH_2HgSC(C_6H_5)_3$, which exists as a discrete monomer and the observation that the mercaptides $Hg(SR)_2$ are monomeric in benzene.[30] Thioethers, however, are known to form at least three types of Hg^{II} halogen complexes.[26b]

In summary, we have provided a mechanistic pathway for the anion exchange of alkylmercury derivatives that involves a bridged species. Our data provide convincing evidence that the rate of anion exchange parallels the bridging capacity of the ligand on mercury. We have also provided another rational pathway for the migration of alkylmercurials in biological systems.

Experimental Section

Elemental analyses were performed by Midwest Microlabs, Inc. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Mass spectra were measured on an AEI MS-902 instrument at 70 eV with an accelerating potential of 8 V. NMR spectra in methylene chloride were run on approximately 0.1 M solutions. Exchange studies were conducted in *N,N*-dimethylformamide (DMF) which first had been distilled and then stored over Linde 4A molecular sieves. The $CHFCl_2$ and $CHClF_2$ were purchased from Union Carbide. Solutions of the appropriate concentrations of two mercurials were prepared, with either cyclopentane or tetramethylsilane as internal standards, and were sealed off in NMR tubes after degassing. Variable-temperature NMR spectroscopy was performed on a Varian A-60A spectrometer equipped with a Varian variable-temperature probe. Temperatures were calibrated using methanol or ethylene glycol according to the improved formula of Van Geet.[31] For those temperatures below −100 °C a copper-constantan thermocouple using a Leeds and Northrup 8690 2-mV potentiometer was employed. Chemical shifts and coupling constants were determined by standard audio frequency side-band techniques and for DMF solutions the temperature dependence of the chemical shifts of each methylmercury compound was measured independently.

Theoretical spectra were generated by an IBM 360/67 computer and plotted on a Calcomp plotter using a program of Raban and Carlson[32] based on the solution to the exchange-modified Bloch equations (program CLAS). The determination of rates of exchange by total line-shape analysis involved obtaining complete correspondence between experimental and theoretical spectra. In general, for a pair of species A and B of equal concentrations the rate of exchange $= (1/[A])(d[A]/dt) = 1/\tau$ and for this process the exchange rate $= k_2[A][B]$, $1/\tau_A = k_2[B]$, and $1/\tau_B = k_2[A]$. The entropy and enthalpy of activation were calculated using a double-precision linear least-squares computer program of the Eyring equation with

$$\ln\frac{k}{T} = \ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} - \left(\frac{\Delta H^{\ddagger}}{R}\right)\left(\frac{1}{T}\right)$$

Rate constants for each exchange system were evaluated at a minimum of eight temperatures. For each system a correlation coefficient of at least 0.998 was obtained for the Eyring plot.

Methylmercury Acetate (2a). Methylmercury acetate was purchased from Alfa-Ventron and recrystallized from absolute ethanol, yielding a white powder: mp 124–125 °C; NMR (CH_2Cl_2) δ 1.04 (s, 3, ^2J = 212.1 Hz) and 1.95 (s, 3). The mass spectrum for each of the compounds given below list the more intense ions giving: ion *m/e*, suggested structure of the fragment, (% intensity relative to Hg^+). The observed *m/e* values for mercury containing fragments exhibited the six mercury isotopes from 198 to 204 amu. For simplicity, only *m/e* values corresponding to ^{202}Hg, ^{35}Cl, and ^{79}Br are given, although the percent intensities were calculated using the sum of all the contributing isotopes present for each fragment. Mass spectrum *m/e* 276, $CH_3HgOC(=O)CH_3^+$ (7.7); 261, $HgOC(=O)CH_3^+$ (62.0); 232, $(CH_3)_2Hg^+$ (6.4); 217, CH_3Hg^+ (265); 202, Hg^+ (100); 101, Hg^{2+} (8.7); 60, $HOC(=O)CH_3^+$ (5.6); 43, CH_3CO^+ (8.5); 42, $CH_2{=}C{=}O^+$ (6.4).

Methylmercury Chloride (2b). Methylmercury chloride was prepared by the standard Grignard method[33] and recrystallized from methanol to give white platelets: mp 168–169 °C; NMR (CH_2Cl_2) δ 1.09 (s, ^2J = 205.2 Hz); mass spectrum *m/e* 252, CH_3HgCl^+ (80); 237, $HgCl^+$ (21.4); 217, CH_3Hg^+ (67); 202, Hg^+ (100); 101, Hg^{2+} (9.7); 49, CH_2Cl^+ (3.9); 36, HCl^+ (7.2); 35, Cl^+ (3.2).

Methylmercury Thiocyanate (2c). Methylmercury thiocyanate was obtained by reaction of methylmercury iodide and excess silver thiocyanate in ethanol and recrystallized from methanol: mp 123–124 °C; NMR δ 1.21 (s, ^2J = 192.0 Hz); mass spectrum *m/e* 275, CH_3HgSCN^+ (33); 260, $HgSCN^+$ (9); 243, CH_3HgCN^+ (8.2); 234, HgS^+ (8.7); 217, CH_3Hg^+ (155); 202, Hg^+ (100); 73, CH_3SCN^+ (24); 58, SCN^+ (7.3).

Methylmercury Bromide (2d). Methylmercury bromide was made by the Grignard method and recrystallized from methanol to give white platelets: mp 158–160 °C; NMR (CH_2Cl_2) δ 1.19 (s, ^2J = 198.8 Hz); mass spectrum *m/e* 296, CH_3HgBr^+ (22.3); 281, $HgBr^+$ (39.5); 232, Me_2Hg^+ (4.9); 217, CH_3Hg^+ (73); 202, Hg^+ (100); 101, Hg^{2+} (18); 93, CH_3Br^+ (4.7); 92, CHBr (2.8); 79, Br^+ (1.7); 80, HBr^+ (1.4).

Methylmercury Cyanide (2e). Methylmercury cyanide was obtained by the anion exchange reaction between potassium cyanide and methylmercury acetate and recrystallized from 1:1 benzene/hexane as white granules: mp 91–93 °C; NMR (CH_2Cl_2) δ 0.88 (s, ^2J = 171.4 Hz); mass spectrum *m/e* 243, CH_3HgCN^+ (31); 228, $HgCN^+$ (12.2); 232, $Hg(CH_3)_2^+$ (0.8); 217, CH_3Hg^+ (114); 202, Hg^+ (100); 142 (0.8); 101, Hg^{2+} (7.2); 93 (1.3); 41, CH_3CN^+ (1.7); 40, CH_2CN^+ (3.6); 27, HCN^+ (18); 26, CN^+ (3.7).

Methylmercury Thioacetate (2f). Methylmercury chloride (2.5 g, 10 mmol), thioacetic acid, (0.76 g, 10 mmol), 50 ml of methanol, and 10 ml of 1 M aqueous NaOH (10 mmol) were combined as described above. Evaporation of solvent led to a greyish solid which was purified by recrystallization from methylene chloride to give 1.25 g (43%) of a white solid: mp 138–140 °C; NMR (CH_2Cl_2) δ 0.92 (s, 3, ^2J = 167.4 Hz), 2.38 (s, 3).

Methylmercury Methylmercaptoacetate (2g). To a stirred solution of 1.25 g (5 mmol) of CH_3HgCl and 1.7 ml of 3 N NaOH (5.1 mmol) in 25 ml of CH_3OH was added 0.53 g of $HSCH_2COOCH_3$ in 10 ml of CH_3OH. After 5 min the product was extracted with ether from a saturated NaCl solution. Removal of the ether afforded a pale yellow oil that had NMR (CH_2Cl_2) δ 0.83 (s, 3, ^2J = 164.0 Hz) and 3.72 (s, 5).

Methylmercury *p*-Chlorophenylmercaptide (2h). To a solution of 0.5 g (2.0 mmol) of MeHgCl in 20 ml of hot methanol was added a warm solution of 0.29 g of *p*-chlorophenylmercaptan (2.0 mmol) in 10 ml of MeOH and 1 ml of 5 N aqueous NaOH. Excess NaOH solution was added until a white precipitate formed and remained. The solution was then heated to boiling and a crystalline precipitate formed on cooling. Filtration gave 0.61 g (85%) of crude product. Recrystallization from methylene chloride gave white needles: mp 63–65 °C; NMR (CH_2Cl_2) δ 0.92 (s, 3, ^2J = 161.7 Hz), 7.24 (m, 4). Anal. Calcd for C_7H_7HgSCl: C, 23.40; H, 1.96. Found: C, 23.44; H, 2.07. Mass spectrum *m/e* 360, $CH_3HgSC_6H_4Cl^+$-*p* (146); 217, CH_3Hg^+ (100); 202, Hg^+ (100); 101, Hg^{2+} (16.2); 158, $CH_3SC_6H_4Cl^+$-*p* (45); 151 (76); 144, $HSC_6H_4Cl^+$-*p* (103); 143, $SC_6H_4Cl^+$-*p* (224); 109, $SC_6H_5^+$ (33.5); 108, $SC_6H_4^+$ (108); 99, $SC_5H_7^+$ (30.4).

Methylmercury Phenylmercaptide (2i). A solution of 2.2 g (8.8 mmol) of MeHgCl in 50 ml of methanol was combined with an equivalent amount of aqueous 2 N NaOH (4.4 ml). After stirring for 1 h, the solution was filtered and 0.97 g (8.8 mmol) of phenylmercaptan was added to the filtrate. On addition of the mercaptan a white precipitate formed immediately. The solution was stored at 5 °C for 2 h and then filtered to yield 2.5 g (87%) of crude product. Recrystallization from methylene chloride afforded white needles: mp 91–92 °C [lit. 92 °C[11b]]; NMR (CH_2Cl_2) δ 0.89 (s, 3, ^2J = 161.5 Hz), 7.24 (m, 5). Anal. Calcd for C_7H_8HgS: C, 25.80; H, 2.78. Found: C, 25.74; H, 2.55. Mass spectrum *m/e* 326, $CH_3HgSC_6H_5^+$ (77); 217, CH_3Hg^+ (59); 202, Hg^+ (100); 101, Hg^{2+} (26); 110, $C_6H_5SH^+$ (181); 109, $C_6H_5S^+$ (40); 78, $C_6H_6^+$ (13.4); 77, $C_6H_5^+$ (17.4); 66, $C_5H_6^+$ (45); 48, $HSCH_3^+$ (80).

Methylmercury Triphenylmethylmercaptide (2j). Methylmercury chloride (1.25 g, 5.0 mmol) was dissolved in 30 ml of methanol. To this solution was added a slurry composed of 1.38 g (5.0 mmol) of triphenylmethylmercaptide, 10 ml of aqueous 1 N NaOH (10 mmol), and 30 ml of methanol. The resulting solution was stirred with warming until the formation of a gray suspension was noted. After 30 min at 25 °C, the solvent was evaporated and the crude gray mass was dissolved in benzene, filtered through $MgSO_4$, concentrated, and cooled. The large clear crystals, 1.35 g (55%): mp 167–169 °C dec; NMR (CH_2Cl_2) δ 0.41 (s, 3, ^2J = 159.8; Hz), 7.30 (m, 15). Anal.

Calcd for $C_{20}H_{18}HgS$: C, 48.92; H, 3.69. Found: C, 48.89; H, 3.83.

Methylmercury Methylmercaptide (2k). Employing a variation of the method of Nyguist and Mann,[4] methylmercaptan (2.2 ml, 39 mmol) was condensed into a small tube immersed in dry ice and subsequently distilled through a gas bubbler into a solution of 9.0 g (36 mmol) of MeHgCl in 19 ml of 2 N aqueous NaOH (38 mmol) and 60 ml of absolute methanol. The mixture was allowed to stand overnight at 0 °C, affording a white precipitate which was a clear viscous oil at room temperature. Water (~10 ml) was added to the mixture which then was extracted with pentane (4 × 50 ml). Evaporation of pentane from the combined extracts afforded 8.2 g (87%) of crude product. Further purification was achieved by high-vacuum distillation: mp 24–25 °C [lit. 25 °C[4]]; NMR (CH_2Cl_2) δ 0.82 (s, 3, ^2J = 157.1 Hz), 2.41 (s, 3). Anal. Calcd for C_2H_6HgS: C, 9.14; H, 2.30. Found: C, 9.25; H, 2.48. Mass spectrum *m/e* 262, $CH_3HgSCH_3^+$ (42); 249, CH_3HgS^+ or $HgSCH_3^+$ (12); 232, $(CH_3)_2Hg^+$ (6.6); 217, CH_3Hg^+ (39); 202, Hg^+ (100); 101 Hg^{2+} (24); 48, $HSCH_3^+$ (13); 47, CH_3S^+ (67); 46, $CH_2{=}S^+$ (11), 45, $HC{=}S^+$ (19).

Bis(methylmercury) Sulfide (2l). This compound was prepared by the procedure of Grdenic.[34] The crude product was recrystallized from benzene to give a white solid (60%); mp 141–143 °C dec [lit.[34] 144 °C dec]; NMR (CH_2Cl_2) δ 0.77 (s, ^2J = 156.6 Hz); mass spectrum *m/e* 466 ($C_2H_6Hg_2S$).

Methylmercury Benzylmercaptide (2m). To a solution of CH_3HgCl (0.50 g, 2.0 mmol) and 0.08 g of NaOH in 30 ml of CH_3OH was added 0.248 g (2.0 mmol) of $C_6H_5CH_2SH$. After stirring for 15 min, 10 ml of H_2O was added and the product was extracted with three 30-ml portions of pentane. Removal of solvent afforded 0.67 g (99%) of crude product as a clear dense oil: NMR (CH_2Cl_2) δ 0.57 (s, 3, ^2J = 156.6 Hz), 4.17 (s, 2), 7.305 (m, 5). Anal. Calcd for $C_8H_{10}HgS$: C, 28.36; H, 2.98. Found: C, 28.66; H, 3.14. Mass spectrum *m/e* 340, $CH_3HgSCH_2C_6H_5^+$ (344); 217, CH_3Hg^+ (56); 202, Hg^+ (100); 123, $SCH_2C_6H_5^+$ (373); 121, $SC_7H_5^+$ (54); 92, $H_3CC_6H_5^+$ (94); 91, $H_2CC_6H_5^+$ (448); 77, $C_6H_5^+$ (60); 65, $C_5H_5^+$ (127); 63, $C_5H_3^+$ (52); 51, $C_4H_3^+$ (52); 45, SCH^+ (149).

Methylmercury Mesitylmercaptide (2n). This compound was prepared from methylmercury chloride (0.33 M) and mesitylmercaptan by the procedure described above. Upon addition of the mercaptan a white precipitate formed. Extraction of the aqueous methanol solution with methylene chloride, removal of the solvent, and recrystallization from CH_2Cl_2/MeOH solution afforded a white fibrous solid (70%): mp 122–124 °C; NMR (CH_2Cl_2) δ 0.77 (s, 3, ^2J = 156.0 Hz), 2.28 (s, 3), 2.53 (s, 6), 6.92 (m, 2). Anal. Calcd for $C_{10}H_{14}HgS$: C, 32.73; H, 3.85. Found: C, 33.01; H, 4.00. Mass spectrum *m/e* 368, $CH_3HgSC_9H_{11}^+$ (605); 217, CH_3Hg^+ (64); 202, Hg^+ (100); 101, Hg^{2+} (26.5); 153, $H_2SC_9H_{11}^+$ (100); 152, $HSC_9H_{11}^+$ (306); 151, $SC_9H_{11}^+$ (1890); 119, $C_9H_{11}^+$ (170); 107, $C_8H_{11}^+$ (290); 105, $C_8H_9^+$ (266); 91, $C_7H_7^+$ (195); 77, $C_6H_5^+$ (125); 65, $C_5H_5^+$ (85); 59, $SC_2H_3^+$ (115); 51, $C_4H_3^+$ (80); 45, SCH^+ (360); 41, $C_3H_5^+$ (80).

Methylmercury *tert*-Butylmercaptide (2p). Methylmercury chloride (2.5 g, 10 mmol) and *tert*-butylmercaptan (0.90 g, 10 mmol) were dissolved in a methanolic solution containing 5 ml of 3 M aqueous NaOH as described above. Distilled water (~15 ml) was added until a lasting cloudiness developed. After the mercurial solution was extracted with pentane (2 × 25 ml), 20 ml of water and 15 ml of 3 N NaOH were added to the aqueous methanol and it was again extracted with pentane (4 × 25 ml). The pentane was removed, affording a crude solid which on sublimation (40 mm, 25 °C) afforded 2.70 g (89%) of a white granular solid; mp 41–42 °C; NMR (CH_2Cl_2) δ 0.77 (s, 3, ^2J = 150.2 Hz), 1.48 (s, 9). Anal. Calcd for $C_5H_{12}HgS$: C, 19.70; H, 3.97. Found: C, 19.37; H, 3.99. Mass spectrum *m/e* 306, $CH_3HgSC(CH_3)_3^+$ (36); 291, $HgSC(CH_3)_3^+$ (11); 217, $MeHg^+$ (29.5); 202, Hg^+ (100); 101, Hg^{2+} (24); 90, $HSC(CH_3)_3^+$ (17.3); 57, $C(CH_3)_3^+$ (44); 56, $C_4H_8^+$ (50); 55, $C_4H_7^+$ (31); 47, SCH_3^+ (20.5); 41, $C_3H_5^+$ (167).

***tert*-Butylmercuric Chloride (4a).** The compound was prepared from *tert*-butyl chloride and $HgCl_2$. Recrystallization from CH_3OH afforded white needles: mp 128–130 °C; NMR (CH_2Cl_2) δ 1.58 (s, ^3J = 256.4 Hz); mass spectrum *m/e* 294, $C_4H_9HgCl^+$ (1.8); 279, $C_3H_6HgCl^+$ (4.7); 259, $C_4H_9Hg^+$ (1.53); 237, $HgCl^+$ (8.6); 202, Hg^+ (100); 101, Hg^{2+} (8.3); 58, $C_4H_{10}^+$ (10.4); 57, $C_4H_9^+$ (278); 56, $C_4H_8^+$ (47); 55, $C_4H_7^+$ (31); 43, $C_3H_7^+$ (10.4); 42, $C_3H_6^+$ (13); 41, $C_3H_5^+$ (153).

***tert*-Butylmercury Methylmercaptide (4b).** The compound was prepared from 0.59 g (2.0 mmol) of $(CH_3)_3CHgCl$, 1 ml of 3 N NaOH, and 0.13 ml of CH_3SH (2.4 mmol) in 40 ml of CH_3OH at −78 °C. The reaction mixture was allowed to stir for 30 min at 25 °C and the product was recovered by extraction into pentane. The pentane was dried ($MgSO_4$), concentrated, and on standing at 0 °C, 0.36 g (59%) of large clear prisms were obtained: mp 56–57 °C; NMR (CH_2Cl_2) δ 1.41 (s, 9, ^3J = 183.0 Hz), 2.32 (s, 3). Anal. Calcd for $C_5H_{12}HgS$: C, 19.70; H, 3.97. Found: C, 19.60; H, 3.95.

***tert*-Butylmercury *tert*-Butylmercaptide (4c).** *tert*-Butylmercury chloride (0.58 g, 2.0 mmol) was dissolved in 30 ml of MeOH and 4 ml of aqueous 1 N NaOH (4.0 mmol). *tert*-Butylmercaptan (0.20 g, 2.2 mmol) was added and the mixture was stoppered and stirred for 1.5 h. After crystals had begun to form the solution was stored overnight in the refrigerator. The crude product, 0.5 g, (72%) was collected by filtration and recrystallized from ethyl ether to give a white solid: mp 56–57 °C; NMR (CH_2Cl_2) δ 1.46 (s, 9, ^3J = 180.8 Hz), 1.43 (s, 9). Anal. Calcd for $C_8H_{18}HgS$: C, 27.70; H, 5.23. Found: C, 27.71; H, 5.29. Mass spectrum *m/e* 348, $C_8H_{18}HgS^+$ (19); 292, $C_4H_{10}HgS^+$ (4); 202, Hg^+ (100); 101, Hg^{2+} (17); 90, $C_4H_{10}S^+$ (39); 89, $C_4H_9S^+$ (8); 75, $C_3H_7S^+$ (14); 57, $C_4H_9^+$ (124); 56, $C_4H_8^+$ (42); 55, $C_4H_7^+$ 22); 43, $C_3H_7^+$ (11); 42, $C_3H_6^+$ (11); 41, $C_3H_5^+$ (106).

***tert*-Butylmercury Benzylmercaptide (4d).** A solution of *tert*-butylmercury chloride (0.596 g, 2.0 mmol) in 50 ml of methanol was combined with a solution consisting of benzylmercaptan (0.248 g, 2.0 mmol), 12 ml of methanol, and 1 ml of 3 N NaOH. After the resulting solution was stirred for 20 min, it was warmed and water (5.5 ml) was added until a permanent cloudiness persisted. The solution was heated until clear and then stored in the freezer. The crude product was collected by filtration and 0.74 g (97%) of product was recrystallized from pentane to give white needles: mp 75–76 °C; NMR (CH_2Cl_2) δ 1.22 (s, 9, ^3J = 188.4 Hz), 4.13 (s, 2), 7.305 (m, 5). The compound was unstable in the presence of light.

***tert*-Butylmercury *p*-Nitrophenylmercaptide (4e).** A solution of 0.295 g of *tert*-butylmercury chloride (1 mmol) in 20 ml of methanol containing *p*-nitrophenylmercaptan (0.17 g of 80% purity) and 0.7 ml of 3 N NaOH in 20 ml of methanol rapidly afforded a light colored precipitate. After the solution was refrigerated overnight, it was filtered to yield 0.35 g (85%) of crude solid, which on recrystallization from CH_2Cl_2 pentane (1:1) gave yellow platelets: mp 135–137 °C dec; NMR (CH_2Cl_2) δ 1.50 (s, 9, ^3J = 212.2 Hz), 7.8 (m, 4).

***tert*-Butylmercury α-Methylbenzylmercaptide (4f).** The reaction of $(CH_3)_3CHgCl$ (1 mmol) and $HSCH(CH_3)C_6H_5$ in basic CH_3OH afforded 0.35 g (85%) of crude product. Recrystallization from cyclopentane afforded white needles: mp 71–73 °C; NMR ($CDCl_3$) δ 1.18 (s, 9, ^3J = 189.8 Hz), 1.72 (d, 3, J = 7.0 Hz), 4.65 (q, 1, J = 7.0 Hz), 7.37 (m, 5). Anal. Calcd. for $C_9H_{12}HgS$: C, 36.50; H, 4.59. Found: C, 36.19; H. 4.54.

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Nuclear Magnetic Resonance Studies. 5. Properties of Phosphorus–Carbon Ylides[1]

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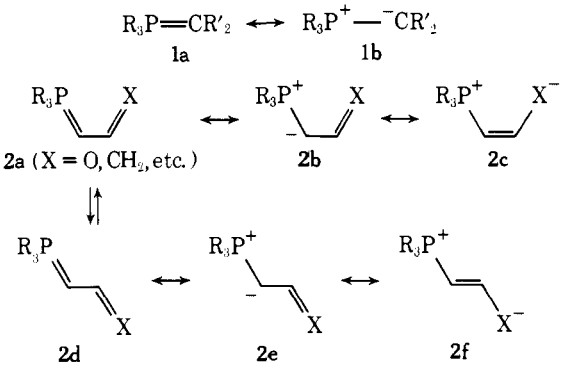
Abstract: The ^{13}C and ^{31}P NMR data for stabilized and nonstabilized phosphorus–carbon ylides are compared to CNDO/2 and MINDO/3 molecular orbital calculations. Evidence of both an experimental and theoretical nature is presented that indicates that the carbon adjacent to phosphorus exists in a trigonal conformation. The molecular orbital calculations predict substantial π interactions between the carbanion and phosphonium group. The various theoretical methods are compared to the trends in ^{13}C and ^{31}P chemical shifts developed for the compounds in this study. It is found that the negative charge in stabilized phosphoranes is delocalized over the π framework of the molecules to a smaller extent than for analogous carbanions. The conformational preferences of ethylidene, cyclopropylidene, allylidene, and formylmethylenephosphorane are studied by theoretical techniques and the results are in agreement with available experimental data.

Ylides occupy a unique position in the chemistry of carbanions, since the gegenion is incorporated in the framework of the molecules. Hence, no ion-pairing effects contribute to its electronic properties or structure. Phosphorus–carbon ylides, in particular, have enjoyed widespread use in synthesis.[4] Thus, these compounds are of considerable interest from the standpoint of their electronic structure and chemical reactivity.

A preliminary account of the carbon NMR of phosphorus ylides has been published.[5] The carbon and phosphorus NMR of methylenetrimethylphosphorane[6] and a series of stabilized phosphoranes[7] (ylides containing strong electron-withdrawing groups adjacent to the carbanion) have also appeared in the literature. This NMR information, as well as recent photoelectron spectroscopy studies on several ylides[8] indicate substantial negative charge on the carbon adjacent to phosphorus. These "carbanions" are, however, by no means unstable. Methylenetrimethylphosphorane can be distilled without decomposition[9] and an x-ray structural determination of methylenetriphenylphosphorane has been carried out.[10] The nonstabilized ammonium ylides, on the other hand, decompose rapidly.[11] The extra stability of phosphoranes compared to their nitrogen counterparts, short P–C bond distances, and numerous other physical properties have led many researchers to the conclusion that there is a multiple bond formed between phosphorus and carbon presumably via $d\pi$–$p\pi$ overlap.[4,12] The involvement of d orbitals in a "chemically significant" manner has been challenged recently.[13,14] Thus, the following resonance structures may be considered to contribute by varying degrees to nonstabilized and stabilized phosphoranes.



In the present work, a qualitative assessment of the importance of resonance structures outlined above is accomplished from two directions. First, by comparison of suitable, closely related compounds (in this case the parent phosphonium salts) the ^{13}C chemical shifts and ^{13}C–^{31}P coupling constants can provide a qualitative estimation of the electronic environment[15] in phosphoranes. This data is supplemented by ^{31}P chemical shifts. Second, CNDO/2[16] and MINDO/3[17] molecular orbital calculations were carried out on model phosphoranes. These calculations lend support for the arguments developed from