prediction[44a] that some falloff with rate should occur, but the effect is far less than predicted by eq 10a. That electron transfer in this region is not yet well understood is illustrated by recent flash photolysis studies which indicate that outer-sphere reactions like $RuB_2(CN)_2^+ + p\text{-}CH_3\text{-}NC_5H_4OCH_3 \rightarrow RuB_2(CN)_2 + p\text{-}CH_3\text{-}N^+C_5H_4OCH_3$ may exceed the diffusion-controlled limit.[41] Using such systems it may be possible to obtain kinetic evidence for long-range electron transfer through intervening solvent molecules for reactions in the abnormal free-energy region.

Most of the applications discussed so far have used $Ru(bpy)_3^{2+*}$ as the excited state. However, the participation of metal-complex excited states in electron-transfer reactions appears to be a general phenomenon with widespread opportunities for exploitation. Electron-transfer quenching has been shown to occur for a series of CT states ($[Ru(trpy)(bpy)(NH_3)]^{2+}$, etc.),[45,46] and for f–f ($Eu(phen)_3^{3+}$)[45] and π–π^* (Pd(OEP); OEP is octaethylporphyrin)[45] excited states. All of these examples have relied on the observation of luminescence as an indication for the existence of an excited state. The use of excited states as electron-transfer reagents may be far more widespread. Recent work has shown that even nonemitting excited states can be quenched at high quencher concentrations (e.g., reaction 31–33 in DMF; TPP is tetraphenylporphine),

$$Ru(TPP)(py)_2 \xrightarrow{h\nu} Ru(TPP)(py)_2^* \quad (31)$$

$$Ru(TPP)(py)_2^* + Ru(NH_3)_6^{3+} \rightarrow Ru(TPP)(py)_2^+ + Ru(NH_3)_6^{2+} \quad (32)$$

$$Ru(TPP)(py)_2^+ + Ru(NH_3)_6^{2+} \rightarrow Ru(TPP)(py)_2 + Ru(NH_3)_6^{3+} \quad (33)$$

and excited-state lifetimes can be estimated by observing product yields as a function of quencher concentration.[47] The full range and extent of excited state electron transfer reactivity is probably just beginning to appear.

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Concluding Remarks

Although often discussed separately and treated using different formalisms, charge transfer, thermal electron transfer, and intervalence transfer are obviously conceptually related processes and many of the ideas developed here should apply to all three. For example, in charge transfer in $Ru(bpy)_3^{2+}$, $Ru^{II}B_3^{2+} + h\nu \rightarrow Ru^{III}(B_3^{-}\cdot)^{2+*}$, and in intervalence transfer in an unsymmetrical mixed-valence ion, $[(NH_3)_5Ru^{III}(pyz)\text{-}Ru^{II}Cl(bpy)_2]^{4+} + h\nu \rightarrow [(NH_3)_5Ru^{II}(pyz)Ru^{III}Cl(bpy)_2]^{4+}$, the electron-acceptor sites, ligand vs. metal, are different, but the processes are obviously similar. In the future it may be possible to explore the interrelationships between the three types of processes in detail to the mutual advantage of all three by using specially designed metal complexes and, where appropriate, new developments in short-time resolution spectroscopies. Hopefully, with continued experimental and theoretical advances, a unified treatment of electron transfer will evolve and perhaps the useful exploitation of metal complex excited states will become a reality.

The work of my own described here is really that of my collaborators, and they are mentioned in the references cited. I would especially like to mention our collaboration with my colleague David Whitten and his group on much of the excited-state chemistry. This article was written in part while I was on sabbatical leave at The University of Sydney. I wish to acknowledge the hospitality of Professor Hans Freeman and his colleagues in the Department of Chemistry, exceedingly valuable conversations with Dr. Jim Beattie and Professor Noel Hush, and the W. R. Kenan Foundation, the A. P. Sloan Foundation, and the Department of Inorganic Chemistry at Sydney for sabbatical leave support. Financial support for my work on electron transfer has come from the Army Research Office, Durham, the National Science Foundation, and the Materials Research Center of The University of North Carolina.

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The Aqueous Solution Chemistry of Methylmercury and Its Complexes

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Received March 17, 1977

The importance of methylmercury, CH_3Hg^{II}, in pollution of the environment by mercury became apparent in the 1960s following the surprising discovery that a large fraction of the mercury in fish was methylmercury, even though some of the fish were taken from lakes and rivers into which no methylmercury had been discharged. Subsequent studies of the biological cycle of mercury revealed chemical and microbiological pathways by which CH_3Hg^{II} can be formed from Hg^{II}.[1-3] The realization that methyl-

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0001-4842/78/0111-0100$01.00/0

mercury is a potential threat to public health sparked interest in its chemistry and biochemistry. Our interests have been in the aqueous coordination chemistry of CH_3Hg^{II} and in the role it plays in determining the behavior of CH_3Hg^{II} in biological systems.

CH_3Hg^{II} has a rich coordination chemistry, forming complexes with a variety of organic and inorganic ligands. Yet its coordination chemistry is fascinatingly simple since it almost always complexes with a coordination number of one. Indeed, this simplicity forms the basis for its use as a highly selective reagent for protein sulfhydryl groups and as a chemical probe for unpaired bases in superhelical DNA. The purpose of this Account is to summarize what is known about the aqueous solution chemistry of CH_3Hg^{II} and its complexes with small ligands, to relate it to the behavior of CH_3Hg^{II} in humans, and to indicate where future research in this area might contribute to unraveling the chemical basis of CH_3Hg^{II} poisoning.

Coordination Numbers of CH_3Hg^{II}. Although the mercury of CH_3Hg^{II} has a strong tendency toward linear two-coordination, it does possess some residual Lewis acidity. Schwarzenbach and Schellenberg were the first to provide experimental evidence for higher coordination.[4] An increase in the aqueous solubility of CH_3HgI in KI solution was attributed to the formation of $CH_3HgI_2^-$, for which the formation constant was estimated to be 2. For comparison, the formation constant of CH_3HgI is 4×10^8. Barbieri and Bjerrum also determined from solubility measurements that $C_2H_5HgX_2^-$ and $C_2H_5HgX_3^{2-}$ complexes form with iodide and thiocyanate but found no evidence for the analogous chloride and bromide complexes.[5] For the iodide complexes, $K_2 = 0.215$ and $K_3 = 5.63$; for the thiocyanate complexes, $K_2 = 0.80$ and $K_3 = 1.59$. Inorganic mercury also has a strong tendency toward linear two-coordination; for example, the stepwise formation constants for the HgI_x^{2-x} complexes are: $K_1 = 7.4 \times 10^{12}$, $K_2 = 8.9 \times 10^{10}$, $K_3 = 4.7 \times 10^3$, and $K_4 = 2.3 \times 10^2$.[6] But, by comparison, the residual Lewis acidity of RHgX is small relative to that of HgX_2.

Spectroscopic results indicate that the mercury in $CH_3Hg(SCN)_3^{2-}$ has a distorted tetrahedral coordination, in which the Hg–C bond and one Hg–SCN bond are covalent and the two other Hg–SCN bonds are weaker interactions,[7] perhaps involving overlap of ligand electron pairs with the vacant 6p orbitals of mercury.[8] Of particular interest is the observation that $^2J_{^1H-^{199}Hg}$[9] increases from 205.6 to 220 Hz on going from CH_3HgSCN to $CH_3Hg(SCN)_3^{2-}$.[7] The ^1H–^{199}Hg coupling is due to the Fermi contact interaction wherein the magnitude of J depends on the contribution of the Hg 6s orbital to the Hg–C bond.[10,11] Thus, if the hybridization of the Hg(II) changed from sp to sp^3 with the formation of $CH_3Hg(SCN)_3^{2-}$, J would be expected to decrease considerably. The small increase in the Hg 6s orbital contribution indicated by the small increase in J has been attributed to changes in the effective nuclear charge when the second and third thiocyanate ligands bond.[7] Similar small increases in J have been observed for RHgX and R_2Hg compounds as the electron-donating ability of the solvent increases.[8,11]

CH_3Hg^{II} also has a coordination number greater than one in its complexes with some chelating ligands.[12-16] Of the few examples reported, the 2,2′-bipyridine complex has been characterized most completely. Anderegg found the formation constant of the bipyridine complex to be 7.2×10^5, as compared to 6.3×10^4 for the pyridine complex,[14,17] to provide the first indication of chelation. In the crystal structure, the C,Hg,N,N′ group is planar with unsymmetrically chelated bipyridine and three-coordinate mercury.[15] The C–Hg–N bond angles are 164 (1) and 126 (1)°, with Hg–N bond lengths of 2.24 (3) and 2.43 (3) Å, respectively. J for the 2,2′-bipyridine complex (238.8 Hz) is also slightly larger than that of the unidentate pyridine complex (229.6 Hz), clearly indicating that a Hg sp hybridization scheme describes the Hg–C bonding in both the pyridine and bipyridine complexes.[16] That the small increase in J is due to chelation in the 2,2′-bipyridine complex was demonstrated by the observation that J for the 3,3′-dimethyl-2,2′-bipyridine complex, in which steric interactions between the 3- and 3′-methyl groups prohibit the ligand from having the cis conformation required for chelation, is 230.4 Hz.[16]

It is tempting to suggest that comparison of J values for CH_3Hg^{II} complexes of potentially chelating ligands with those of the appropriate monodentate ligands is a general method for establishing higher coordination in complexes of potentially chelating ligands. Although this is probably so for many cases, J also depends on other factors, such as donor group basicity, which may be difficult to separate from the effect of chelation.

CH_3Hg^{II} Complexes of Inorganic Ligands. The aqueous chemistry of CH_3Hg^{II} is dominated by the acid–base and self-association reactions[4,18,19]

$$CH_3HgOH_2^+ + OH^- \rightleftarrows CH_3HgOH + H_2O \quad (1)$$

$$CH_3HgOH_2^+ + CH_3HgOH \rightleftarrows (CH_3Hg)_2OH^+ + H_2O \quad (2)$$

This model was developed by Schwarzenbach and Schellenberg from pH titration data[4] and, although there has been some controversy[20] due to attempts to extrapolate synthetic results to aqueous solution species and equilibria,[21] it is firmly supported by Raman and NMR spectral data.[18,19,22-24] The species $CH_3HgOH_2^+$

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Table I
Formation Constants of CH_3Hg^{II} and Proton Complexes and $J_{^1H-^{199}Hg}$ for the CH_3Hg^{II} Complexes of Inorganic Ligands[a]

Ligand	Donor atom	$\log \frac{[CH_3HgL]}{[CH_3Hg^+][L]}$	$\log \frac{[HL]}{[H^+][L]}$	$J_{^1H-^{199}Hg}$[b]	Ref[c]
F^-	F	1.50	2.85		4
Cl^-	Cl	5.25	−7	215.2[d]	4,11
Br^-	Br	6.62	−9	212.0[d]	4,11
I^-	I	8.60	−9.5	200.0[d]	4,11
OH^-	O	9.37	15.7	203.0	4,18
CH_3HgOH	O	2.37	4.59	260.0	4,18
SO_4^{2-}	O	0.94	1.04	251.4	27,27
SeO_4^{2-}	O	1.12	2.0	248.5	27,27
CO_3^{2-}	O	6.10	6.5	221.4	27,27
SeO_3^{2-}	O	6.46	8.18	223.5	27,27
CN^-	C	14.1	9.14	178.0[d]	4,11
S^{2-}	S	21.2	14.2	146	4,27
CH_3HgS^-	S	16.3		156[d]	4,27
$(CH_3Hg)_2S$	S	~7		202	4,27
SCN^-	S	6.05		203	4,27
SO_3^{2-}	S	8.11, 7.96	6.79	172.4	4,27
$S_2O_3^{2-}$	S	10.90, 11.05	1.56	191.0	4,18
$SeCN^-$	Se	6.79		200.4	27,27
Se^{2-}	Se			143	27

[a] In H_2O unless indicated otherwise. [b] Hz. [c] The first number is the reference for the formation constant, the second for J. [d] In pyridine solution.

and CH_3HgOH have been identified in aqueous solutions by Raman spectroscopy, and evidence for the dinuclear species has been obtained from Raman spectra of solutions prepared from CH_3HgNO_3 and KOH.

The trinuclear species $(CH_3Hg)_3O^+$ also forms to some extent, as indicated by the precipitation of

$$CH_3HgOH + (CH_3Hg)_2OH^+ \rightleftarrows (CH_3Hg)_3O^+ + H_2O \quad (3)$$

$[(CH_3Hg)_3O]ClO_4$ from concentrated aqueous solutions at neutral pH.[25] The equilibrium constant for its formation is small and in the range 0.3–0.7,[19,26] indicating that the Schwarzenbach and Schellenberg model accounts for all but a small fraction of the CH_3Hg^{II} over the pH range <1 to >13 at CH_3Hg^{II} concentrations < 0.2 M.

Formation constants for the CH_3Hg^{II} complexes of a variety of inorganic ligands are given in Table I.[4,27] Because of the tendency of both CH_3Hg^{II} and the proton to be one-coordinate, it is of interest to compare CH_3Hg^{II} complexes with the corresponding proton complexes. The results in Table I clearly show that CH_3Hg^{II} and H^+ are similar only in the stoichiometry of their association reactions.[4] For the CH_3Hg^{II}–halide complexes we have the stability series $CH_3HgF \ll CH_3HgCl < CH_3HgBr < CH_3HgI$, the opposite of that for the hydrogen halides. Equally striking is the pronounced preference of CH_3Hg^{II} for S derivatives over O derivatives, the reverse of that of the proton. These stability orders and their tendency toward one-coordination classify H^+ and CH_3Hg^{II} as the simplest hard and soft Lewis acids. H^+ is moderately hard, whereas CH_3Hg^{II} is among the softest of the Lewis acids.[28]

The considerable volume of spectroscopic data which has been published on CH_3Hg^{II} complexes has made it possible to identify the ligating atom in those complexes of ambidentate ligands. Proton magnetic resonance and Raman spectroscopy have proven to be particularly useful because of the dependence of J (Table I) and the frequencies of the symmetrical CH_3 deformation and Hg–C stretch vibrations[27] on the nature of the ligating atom. To illustrate, the formation constant of the SO_3^{2-} complex is orders of magnitude larger and J is considerably smaller than the corresponding values for the oxygen-bonded CH_3Hg^{II} in the SO_4^{2-} and SeO_4^{2-} complexes, indicating sulfur bonding in the SO_3^{2-} complex. Further evidence for sulfur bonding comes from Raman data.[27] However, J for the analogous SeO_3^{2-} complex is much larger than that typical for selenium bonding, indicating that, even though the formation constant of the SeO_3^{2-} complex is closer to that of SO_3^{2-} than to those of the SO_4^{2-} and SeO_4^{2-} complexes, oxygen is the ligating atom in the SeO_3^{2-} complex.[27] Oxygen bonding is confirmed by Raman spectroscopy.[27] These results are of interest since selenium (as Na_2SeO_3) decreases the toxicity of CH_3Hg^{II} to rats.[29] From the relative magnitudes of the formation constants of the SeO_3^{2-} complex and those of biological ligands, it is clear that the decreased toxicity must be by some mechanism other than simple sequestering of CH_3Hg^{II} as its selenite complex.

CH_3Hg^{II} Complexes of Organic Ligands. Formation constants have been reported for the CH_3Hg^{II} complexes of a large number of organic ligands.[4,14,17,18,30-32] Complexes of particular interest with respect to the binding of CH_3Hg(II) by biological molecules are listed in Table II. Values of J for some

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Table II
Formation Constants of CH_3Hg^{II} and Proton Complexes and $J_{^1H-^{199}Hg}$ for the CH_3Hg^{II} Complexes of Organic Ligands

Ligand	Donor atom	$\log \frac{[CH_3HgL]}{[CH_3Hg^+][L]}$	$\log \frac{[HL]}{[H^+][L]}$	$J_{^1H-^{199}Hg}$[a]	Ref
Acetic acid	O	3.18	4.65	233.3	18
Acetylglycine	O	2.68	3.40	237.9	18
Dichloroacetic acid	O	1.14	1.00	245.8	18
β-Alanine	O	2.52	3.61	230.5	30
Ammonia	N	7.25	9.32	214.1	30
Methylamine	N	7.57	10.81	211.5	30
Ethylamine	N	7.64	10.82	211.0	30
Dimethylamine	N	6.76	11.02	216.6	30
Trimethylamine	N	5.05	10.05		30
Glycine	N	7.88	9.69	216.0	30
β-Alanine	N	7.56	10.25	213.9	30
4-Aminovaleric acid	N	7.54	10.48	211.9	30
Phenylalanine	N	8.29	9.16		30
Pyridine	N	4.72	5.3	229.6[b]	17
2,2′-Bipyridine	N	5.86	4.44	238.8[b]	14
N-Methylimidazole	N	6.96	7.18	218.8	*c*
Uridine	N-3	9.0	9.2		32
Cytidine	N-3	4.6	4.2		32
Adenosine	N-1	~3	3.5		32
Guanosine	N-1	~8.1	9.2		32
2-Mercaptoethanol	S	16.12	9.52		4
Glutathione	S	15.9	8.93[d]	170.0[e]	17
Cysteine	S	15.7	8.53[f]	174.0[e]	17
Mercaptalbumin	S	22.0			*g*
Methionine	S	1.94		223	31

[a] Hz. [b] Reference 16. [c] C. A. Evans and D. L. Rabenstein, unpublished results. [d] D. L. Rabenstein, *J. Am. Chem. Soc.*, 95, 2797 (1973). [e] Reference 39. [f] R. E. Benesch and R. Benesch, *J. Am. Chem. Soc.*, 77, 5877 (1955). [g] W. L. Hughes, Jr., *Cold Spring Harbor Symp. Quant. Biol.*, 14, 79 (1950).

of the complexes are also given in Table II.

Several correlations have been derived from results of the type given in Table II, the most notable of which is the approximately linear decrease in J as log K increases. The relationship $J = -5.09 \log K + 249$ was obtained from the least-squares analysis of a collection of results somewhat larger than that given in the table.[33] For structurally similar ligands possessing the same ligating group, J also decreases linearly as the Brønsted basicity of the ligand increases.[16,18,34-36] It is of particular interest that Canty and Marker found separate linear correlations between J and ligand pK_A for complexes of unidentate pyridines, bidentate bipyridines, and 1,10-phenanthrolines.[16] The 3,3′-dimethyl-2,2′-bipyridine complex, in which chelation is prevented by steric interaction between the methyl groups, fits the correlation for the unidentate pyridine complexes. For amine complexes, J depends on both the degree of alkyl substitution and the Brønsted basicity of the ligand.[30]

The formation constants cover a wide range of values, depending on the ligand type. In general, they are slightly smaller than those of the corresponding Hg(II) complexes, the difference increasing as the "softness" of the ligand increases. Pearson attributed this to an antisymbiotic effect in which the soft CH_3^- ligand decreases the affinity of Hg for other soft bases.[37]

Although the formation constants of the CH_3Hg^{II} complexes are generally large, the extent to which the complexes form in aqueous solution can be small be-

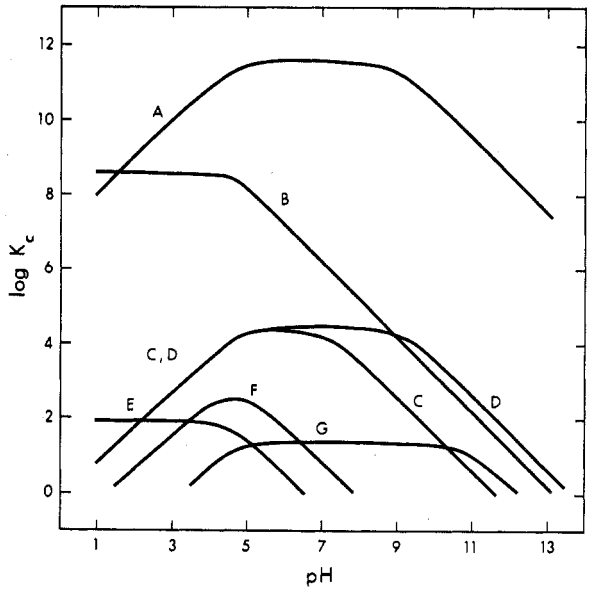

Figure 1. Logarithm of the conditional formation constant[38] vs. pH for CH_3Hg^{II} complexes of: A, glutathione; B, iodide; C, *N*-methylimidazole; D, uridine; E, methionine (sulfur); F, acetic acid; G, methylamine.

cause of competing reactions. At one end of the pH range, protons compete with CH_3Hg^{II} for those ligating groups which are Brønsted bases, while at the other end hydroxide ion competes with the ligand for CH_3Hg^{II}. The effect of competing reactions can be accounted for most easily with conditional formation constants,[38] which for selected complexes are plotted as a function

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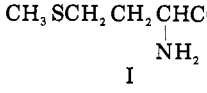
(38) The conditional formation constant, K_c, is defined as the pH-dependent equilibrium constant for the reaction $CH_3Hg_{free} + L_{free} \rightleftarrows CH_3HgL$, where CH_3Hg_{free} and L_{free} include all of the free forms of $CH_3Hg(II)$ and ligand.

of pH in Figure 1. As indicated in Figure 1, K_c is almost always somewhat smaller than the thermodynamic formation constant, and its magnitude is strongly pH dependent.

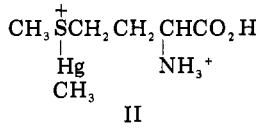
Conditional formation constants show that, of the potential binding sites in biological molecules, the deprotonated sulfhydryl group binds CH_3Hg^{II} most strongly. Even though K_c for the sulfhydryl complex is considerably reduced at the pH extremes, it still is of such a magnitude that the complex forms completely. In accord with this, NMR results indicate complete formation of the CH_3Hg^{II} complexes of cysteine, penicillamine, and glutathione over the pH range 1–13.[39]

Because of the pH dependence of the extent to which it combines with various donor groups, CH_3Hg^{II} is versatile in its binding to polydentate ligands. For example, as predicted by the pH dependence of curves F and G in Figure 1, CH_3Hg^{II} binds to the carboxylate groups of simple amino acids such as glycine at low pH, forming $H_3N^+CH_2CO_2HgCH_3$, while at higher pH the ammonium group is titrated and the complex is $CH_3HgNH_2{}^+CH_2CO_2^-$.[30] At the low and high pH extremes, the complex dissociates due to competing reactions. The type of detailed information about the solution chemistry of such complexes which can be obtained from NMR studies[30,31,39] is illustrated by the methionine system. Methionine (I) has three potential



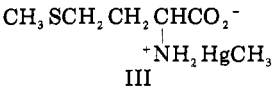
I

binding sites: the thioether group, whose chemical state can be monitored by the chemical shift of the methionine methyl protons, and the amino and carboxylate groups, which together can be monitored by the chemical shift of the methine proton. Chemical shift results indicate that, at pH <2, CH_3Hg^{II} is bonded to the thioether to give II, with no detectable binding to



II

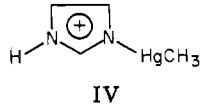
either of the other functional groups. As the pH is increased from 2, CH_3Hg^{II} shifts to the other binding sites and, at pH >8, is bonded exclusively to the amino group (III). Formation constants for the individual



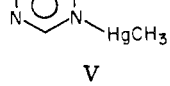
III

complexes have been derived from NMR data.[31] The mode of bonding in III has been confirmed by x-ray crystallography.[13]

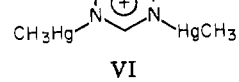
The CH_3Hg^{II}–imidazole system further illustrates the extent to which the nature of CH_3Hg^{II} complexes can depend on pH.[40] Complexes IV–VI form in aqueous



IV



V



VI

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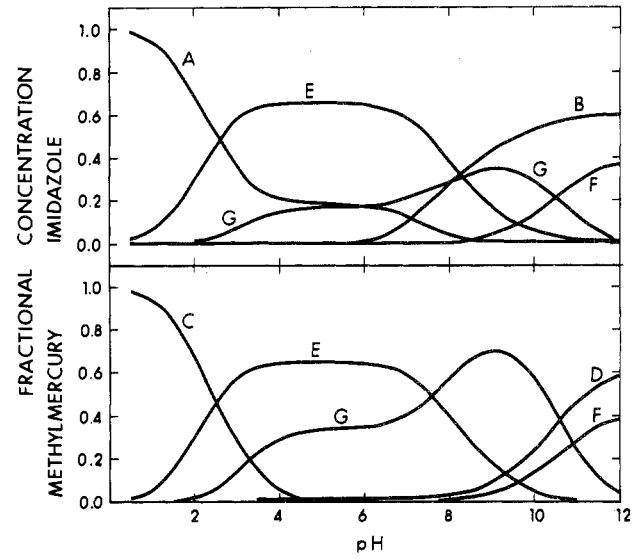

Figure 2. Fractional concentrations of the imidazole- and CH_3Hg^{II}-containing species as a function of pH in a solution containing 0.010 M imidazole and 0.010 M CH_3Hg^{II}: A, H_2Im^+; B, HIm; C, CH_3Hg^+; D, CH_3HgOH; E, CH_3HgHIm^+ (structure IV); F, CH_3HgIm (structure V); G, $(CH_3Hg)_2Im^+$ (structure VI).

solution. As the pH of an equimolar mixture of CH_3Hg^{II} and imidazole is increased, $CH_3Hg(II)$ first binds to the pyridine nitrogen to form IV. Complexation to the pyridine nitrogen in turn causes a considerable increase in the acidity of the proton on the pyrrole nitrogen,[41] which dissociates to form V. Since the stability of CH_3Hg^{II} complexes increases as the basicity of the donor group increases, we have the striking result that, upon deprotonation of IV, the product is consumed (eq 4), giving rise to free imidazole

$$CH_3HgIm + CH_3HgImH^+ \rightleftarrows (CH_3Hg)_2Im^+ + HIm \qquad (4)$$

and to a complex in which imidazolato bridges two CH_3Hg^{II} ions. The pH dependence of the extent to which the complexes form is shown by the fractional concentration curves in Figure 2. The discrete molecular nature of complexes V and VI, a consequence of the strong preference of CH_3Hg^{II} for a coordination number of one, is in marked contrast to the polymeric imidazolato complexes formed by the transition metals.[42]

Whether or not chelation occurs in the amino acid complexes of CH_3Hg^{II} is still an open question. The formation constants of the amino complexes of the homologous series of ligands $H_2N(CH_2)_nCO_2^-$ decrease as n is increased from 1 to 2, whereas the Brønsted basicity increases.[30] Since the formation constants of CH_3Hg^{II} complexes generally increase as the Brønsted basicity of the ligand increases, these results suggest chelation to some extent in the nitrogen-bonded glycine complex. J for the glycine complex is 3 Hz larger than that for the β-alanine complex,[30] consistent with this interpretation. Crystallographic studies have revealed intramolecular mercury–carboxylate oxygen interactions in the sulfhydryl-bonded cysteine complex and in the nitrogen-bonded methionine complex.[13,43] In both

(41) The pK_A of the pyrrole nitrogen decreases from 14.44 to 9.92.[40] For comparison the pK_A of the imidazole complex of aquocobalamin is 10.25 (G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 5694 (1964)).

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complexes the carboxylate interaction causes the C–Hg–X (X = S or N) angle to be slightly less than 180°.[43] However, the interaction must be weak since the Hg···O distances are only slightly less than the sum of the van der Waals radii, and it is not likely to exist in a strongly solvating and hydrogen-bonding aqueous environment. If the carboxylate group is mercury-bonded in the solution phase, J would be expected to decrease as the carboxylate group is protonated and thus prevented from mercury binding. In fact, J increases slightly as the pH is decreased,[39] suggesting that in aqueous solution the bonding involves only the sulfhydryl group. However, protonation of the carboxylate group also causes the pK_A of the sulfhydryl group to decrease, making conclusions based on coupling constant changes ambiguous.

Results for the CH_3Hg^{II}–phenylalanine system suggest another type of interaction by which the stability of some CH_3Hg^{II} complexes can be enhanced.[30] The formation constant of the nitrogen-bonded phenylalanine complex is larger than that for the glycine complex, even though the basicity of the phenylalanine amino group is less. Molecular models show that the methyl group can lie close to the phenyl ring, suggesting that the increased stability may be due to a hydrophobic interaction between the phenyl ring and the methyl group or to a π interaction between the phenyl group and mercury.[30,44] Consistent with this hypothesis, the proton and carbon-13 resonances of the phenylalanine-complexed CH_3Hg^{II} are both ring current shifted, and the shifts are in the direction predicted for the methyl group near the plane of the ring.[30,45]

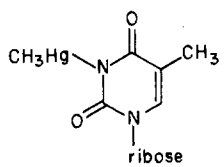
The observation that Hg^{II} compounds denature native DNAs, sometimes reversibly,[46-49] and the recent report that CH_3Hg^{II} causes chromosome damage and consequently is mutagenic[50] have provided the stimulus for detailed studies of the binding of CH_3Hg^{II} by nucleosides, nucleotides, and polynucleotides.[48,51-55] CH_3Hg^{II} can bind at several sites on the base of purine and pyrimidine nucleotides, forming both mono- and polynuclear complexes, depending on the base and the pH. Binding is preferentially to N(1) in purine and to N(3) in pyrimidine nucleosides.[32,48,53] Of the bases, uracil and thymine bind CH_3Hg^{II} most strongly. Binding of CH_3Hg^{II} by adenosine, cytidine, and inosine enhances the CH_3Hg^{II} affinity of other binding sites,[32] presumably due to an increase in the Brønsted basicity from electron delocalization into the ring.[53] Tobias, Mansy, and co-workers have elucidated in detail the nature of numerous CH_3Hg^{II} complexes of nucleosides and nucleotides by Raman difference spectroscopy and have reported results from binding studies on native DNA.[51-55] They propose that CH_3Hg^{II}, in addition to binding to the base, also can bind to the ribose moiety.[51,54] Considering the low stability of CH_3Hg^{II}–phosphate complexes,[56] binding to the phosphate of nucleotides is expected to be weak.

Table III
Rate Constants for Selected CH_3HgL Ligand Exchange Reactions

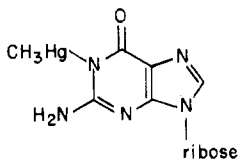
Ligand X	Ligand Y	log k_1[a]	log k_{-1}[a]	log k_2[a,b]	Ref
OH^-	Pyridine	4.6	9.3		62
OH^-	Cl^-	4.4	8.5		61
OH^-	2-PADA[c]	5.4	9.0		61
OH^-	SCN^-	5.79	9.11		61
OH^-	Br^-	5.57	8.32		61
OH^-	I^-	7.15	7.92		61
OH^-	*p*-Nitrophenolate	8.7	5.8		61
OH^-	CN^-	8.9	4.2		59
GS^-	GS^- [d]	8.8	8.8		39
CN^-	SO_3^{2-}	2.8	8.8		59
OH^-	Bipyridine	5.4	8.9		62
H_2O	Br^-	9.7	3.1		61
H_2O	I^-	9.7	1.1		61
H_2O	GSH[d]	9.7			39
H_2O	2-PADA[c]	9.2	3.4		74
CN^-	Cl^-			0.18	63
CN^-	Br^-			0.76	63
CN^-	SCN^-			0.79	63
CN^-	$^-SCH_3$			1.58	63
CN^-	$^-SC_6H_5$			1.60	63
CN^-	$^-SC(CH_3)_3$			1.99	63

[a] M^{-1} s^{-1}. [b] In DMF. [c] Pyridine-2-azo-*p*-dimethylaniline. [d] GSH and GS^- represent the sulfhydryl-protonated and deprotonated forms of glutathione.

It is thought that the first site of reversible binding of CH_3HgOH to DNA is at the deprotonated N(3) of thymidine, VII, followed by N(1) of guanosine, VIII.[48,57]



VII



VIII

In those transfer RNAs containing the modified base, 4-thiouridine, the sulfur of the modified base is the first binding site.[58] Because of its strong preference for unifunctionality, CH_3Hg^{II} is a selective probe for unpaired bases in superhelical DNA.[59]

It is of interest to note the relative position of the curve for CH_3HgI in Figure 1. CH_3HgI is used as a highly specific, monofunctional reagent for protein sulfhydryl groups. Because of its small size and nonaqueous solubility, it can reach otherwise inaccessible sulfhydryl groups located in the interior of proteins, as nicely illustrated by a study of the role of the sulfhydryl groups of fumarase.[60] At physiological pH, the conditional formation constant for the sulfhydryl complex is from 5 to 6 orders of magnitude larger than those for the other complexes, so that the sulfhydryl groups are titrated selectively and quantitatively. The conditional formation constant curves also point out the necessity

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for using CH_3Hg^{II} in the form of its iodo complex.

Dynamics of CH_3Hg^{II} Complexes. Ligand exchange reactions of CH_3Hg^{II} are, in general, extremely fast reactions. The first indication of this came from NMR studies in which exchange-averaged resonance patterns were observed for a variety of CH_3HgX/CH_3HgY mixtures.[11,61] Only when one of the complexes was CH_3HgCN were separate resonances observed for each of the complexes.

Mechanistic studies have elucidated three predominant pathways for ligand exchange: (1) bimolecular nucleophilic attack of Y on CH_3HgX (eq 5), (2) direct

$$CH_3HgX + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3HgY + X \quad (5)$$

bimolecular ligand exchange (eq 6), and (3) proton-

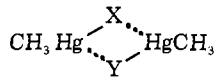
$$CH_3HgX + CH_3^*HgY \overset{k_2}{\rightleftharpoons} CH_3HgY + CH_3^*HgX \quad (6)$$

assisted dissociation of the complex (eq 7). Rate

$$CH_3HgX + H^+ \overset{k_3}{\rightleftharpoons} CH_3Hg^+ + HX \quad (7)$$

constants for examples of types 1 and 2 are given in Table III. Another reaction of importance in the solution dynamics of CH_3Hg^{II} complexes involves metal exchange via a bimolecular electrophilic attack of CH_3Hg^{II} on CH_3HgX. The mechanism presumably involves a dinuclear intermediate, although the details have yet to be elucidated.

Rate data for the nucleophilic exchange pathway indicates an associative reaction mechanism, presumably involving an intermediate of the type



For example, Eigen, Geier, and co-workers have shown that, when X is hydroxide and Y is halide, k_1 is strongly dependent on the particular halide, while k_{-1} is much less so.[62,63] The formation constant of CH_3HgOH is larger than those of the halide complexes, suggesting that once the intermediate forms the tendency for halide dissociation is greater than that for hydroxide dissociation. In support of this hypothesis, when K_{CH_3HgX} is larger than K_{CH_3HgY}, k_1 is less than k_{-1}, and both k_1 and K_{CH_3HgY} increase in the same order; when K_{CH_3HgX} is less than K_{CH_3HgY}, the reverse is true. When $K_{CH_3HgY} >> K_{CH_3HgX}$, k_1 approaches values characteristic of largely diffusion controlled reactions.

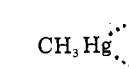
Even though bipyridine and several related ligands form chelates with CH_3Hg^{II}, the dynamics of their complexes are similar to those for complexes of the unidentate ligands,[64] consistent with the idea that binding to the second nitrogen is very weak.[16]

The rate constant in Table III for exchange of glutathione between its free and CH_3Hg^{II}-complexed forms

$$CH_3HgSG + G\overset{*}{S}^- \overset{k_1}{\rightleftharpoons} CH_3Hg\overset{*}{S}G + GS^- \quad (8)$$

via attack by sulfhydryl-deprotonated glutathione[39] is of particular interest with respect to the mobility of CH_3Hg^{II} in biological systems. It also is noteworthy that the analogous reaction involving sulfhydryl-protonated glutathione is slow on the NMR time scale ($k_1 < 0.1\ M^{-1}\ s^{-1}$),[39] as is exchange via nucleophilic attack of $(CH_3)_3CSH$ on $CH_3HgSC(CH_3)_3$ in *o*-dichlorobenzene solvent.[65]

The direct exchange of ligands in CH_3HgX/CH_3HgY mixtures is thought to proceed through a four-center, bridged transition state[65,66]



The rate of exchange in the system CH_3HgX/CH_3HgCN increases as K_{CH_3HgX} increases to the extent that sulfhydryl ligands, which form the thermodynamically most stable complexes, also exchange the most rapidly.[65] The relative rates of direct exchange reflect the bridging ability of the ligands, with the result that the exchange reaction is extremely rapid when both X and Y are sulfhydryl ligands. For example, Bach and Weibel report k_2 for the $(CH_3)_3CHgSCH_3$/$(CH_3)_3CHgSCHCH_3C_6H_5$ system in $HCF_2Cl/HCFCl_2$ solvent to be $3 \times 10^7\ M^{-1}\ s^{-1}$ at 25 °C.[65] Although there are no quantitative results from which to judge the importance of direct ligand exchange in aqueous solution, the absence of three-bond coupling between ^{199}Hg and ligand protons (Hg–S–C–H) in ^1H NMR spectra of CH_3Hg^{II} complexes of glutathione and cysteine and in exchange-averaged resonance patterns for CH_3Hg^{II} in CH_3Hg(glutathione)/CH_3Hg(cysteine) mixtures indicates it to be fast on the NMR time scale ($k_2 > 0.1\ M^{-1}\ s^{-1}$).[39]

Conclusions

Now that the main features of the aqueous solution chemistry of CH_3Hg^{II} and its complexes with small ligands have been elucidated, it is possible to explain some aspects of the behavior of CH_3Hg^{II} in biological systems.[67] For example, formation constants indicate that essentially all the CH_3Hg^{II} will be complexed by sulfhydryl ligands. The only exception is in the stomach, where the conditions of low pH and high chloride concentration favor the formation of a small amount of CH_3HgCl.[68] It is possible that the lipid-soluble CH_3HgCl is involved in the very efficient absorption of CH_3Hg^{II} into the blood stream.[69] In the blood and other organs, CH_3Hg^{II} is distributed among the various sulfhydryl molecules.[70] At first it seemed surprising that the sulfhydryl complexes are so labile since they are so stable thermodynamically. However, we now know that the CH_3Hg^{II}–glutathione model system is labile due to extremely rapid nucleophilic ligand displacement reactions.[39] Clearly, these rapid ligand exchange reactions are the key to the bioavailability of CH_3Hg^{II}[68] and play the same essential role in the treatment of CH_3Hg^{II} poisoning with chemotherapeutic agents which complex it in a more rapidly eliminated form.[71,72]

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It also seems likely that the coordination chemistry of CH_3Hg^{II} holds the explanation for other still unexplained aspects of its behavior in biological systems. For example, some of the CH_3Hg^{II} in the blood enters the brain, the target organ in methylmercury poisoning, where it causes lysis of cells of the central nervous system.[70] If the biocomplexes involved can be identified, it may be possible to determine if the membrane is the primary point of attack or if lysis results indirectly by an inhibition of enzymes or other proteins whose function is essential for the integrity of the membrane. Because of the lability of CH_3Hg^{II} complexes, identification of the biocomplexes will be difficult by conventional homogenization techniques which cause disruption of subcellular compartmentalization and which thus expose the CH_3Hg^{II} to other sulfhydryl ligands. Considering the abundance of sulfhydryl groups, there must be a high degree of selectivity in binding for CH_3Hg^{II} to be able to seek out the target molecules. For example, there is a 4800- to 8000-fold excess of sulfhydryl groups in blood at the CH_3Hg^{II} levels at which toxic symptoms first appear.[70] Factors giving rise to the selectivity are as yet unknown; however, the enhanced stability of the phenylalanine complex may provide a clue.[30] It also seems reasonable to predict that a detailed understanding of the ligand structural features which result in chelation to CH_3Hg^{II} will provide not only some insight into the apparent selectivity of the binding of CH_3Hg^{II} by bioligands but also some guidance in the design of chemotherapeutic agents for the treatment of methylmercury poisoning.

It is a pleasure to acknowledge the contributions of my coworkers, C. A. Evans, M. T. Fairhurst, M. S. Greenberg, S. Libich, R. Ozubko, C. Suvanprakorn, and M. C. Tourangeau. Financial support has been provided by the National Research Council of Canada and the University of Alberta. I also am indebted to Professor R. J. P. Williams and his group at the University of Oxford, where this Account was written during a sabbatical leave.

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Vinyl Triflate Chemistry: Unsaturated Cations and Carbenes

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Received January 28, 1977

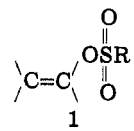
There are essentially four simple carbon species that are major intermediates in organic chemistry: carbanions, radicals, carbonium ions,[1] and carbenes (Table I). Of these four types, vinyl carbanions and radicals have long been known, and their chemistry is understood almost as well as for their saturated analogues. However, vinyl cations and unsaturated carbenes have only recently been investigated.

Among numerous reasons for the long delay in attention to vinyl cations and alkylidenecarbenes, two stand out: (a) vinyl cations were long regarded as unattractive reaction inermediates[2] because of their alleged high energy, and (b) until recently there were no good precursors for their generation. Pioneering work in the 1950s and early 1960s showed that both vinyl cations and unsaturated carbenes are energetically accessible. Hence the full development of the chemistry of these novel intermediates hinged only on the availability of simple and general progenitors.

Table I
Simple Reactive Intermediates of Carbon

Intermediate	Structure	Corresponding unsaturated species
Carbanion	$\geq C^-$	$>C=\bar{C}-$ Vinyl anion
Radical	$\geq C\cdot$	$>C=\dot{C}-$ Vinyl radical
Cation	$\geq C^+$	$>C=C^+-$ Vinyl cation
Carbene	$>C:$	$>C=C:$ Methylenecarbene

It was in connection with the quest for such progenitors that vinyl sulfonate esters (**1**) and vinyl tri-



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fluoromethanesulfonates (**1**, R = CF_3, triflate) attracted our attention. Trifluoromethanesulfonic acid, CF_3SO_3H, first reported by Haszeldine and Kidd,[3] can be manufactured by electrolysis[4] and is a commercially

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