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Methylmercuration of Carbon-Donor Ligands. A Kinetic Preference for Methylmercury(II) Transfer over Proton Transfer

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Received October 26, 1978

Several kinetic and equilibrium aspects of the methylmercuration of deprotonated carbon-acid ligands, L, are investigated in aqueous solution. Ligand protonation is thermodynamically favored over methylmercuration with $\log K_{CH_3HgL} = 0.8\mathrm{p}K_a^{HL}$, however, a distinct kinetic preference for methylmercuration is observed. A comparison of the Brønsted plots for methylmercury transfer and proton transfer to the γ-carbon atom of the macrocyclic tetraazadiene complex $[Ni([14]dienoN_4)]^+$ shows that the transition of α from 1 to 0 is sharper for the CH_3Hg^{II} transfers. The atom-transfer reactions are discussed in terms of Marcus' theory, and it is proposed that the reorganizational energy barrier is smaller for the methylmercury transfers because methylmercury(II) forms more stable bridges than does the proton.

Introduction

The ability of methylmercury to form complexes in aqueous solution with a wide variety of ligands containing P-, S-, N-, and O-donor atoms is well established.[1-4] In addition, the kinetics of the methylmercury-transfer reaction (eq 1) has been

$$L + CH_3HgX \underset{}{\overset{k_{12}}{\rightleftharpoons}} CH_3HgL + X \qquad (1)$$

investigated for a number of ligands.[4-8] This reaction proceeds by an associative mechanism,[4-7] and the forward rate constant, k_{12}, depends on the value of the equilibrium constant, K_{12}, of reaction 1. The dependence of k_{12} on the equilibrium constant is very similar in appearance to that observed for the protonation rate constant, k_{12}', of the analogous reaction (2).[4,5]

$$L + HX \overset{k_{12}'}{\rightleftharpoons} HL + X \qquad (2)$$

In both cases the dependence of $\log k_{12}$ on $\log K_{12}$ is nonlinear. For strongly endergonic reactions ($\log K_{12} < 0$) the slope of a plot of $\log k_{12}$ vs. $\log K_{12}$ is 1. This slope gradually decreases as $\log K_{12}$ increases, and it approaches 0 for reactions which are strongly exergonic. When reaction 1 or 2 is thermodynamically favored ($\log K >> 0$), the rate constants k_{12} and k_{12}' approach the diffusion-controlled limit. This similarity between the methylmercury and proton-transfer reactions is valid for all ligands which are "normal" in the sense that their protonation reactions are rapid in the vicinity of $\log K_{12}' = 0$. The slope of a plot of $\log k_{12}$ vs. $\log K_{12}$ shows a smooth transition from 1 to 0, and, as is the case for the proton, the sharpness of this transition depends on the nature of the ligands L and X.[4,5,7] When L is a sulfur donor, the change in slope from 1 to 0 is very sharp, while it is more gradual when L is the hydroxide ion.[5]

The proton-transfer reactions of many, although not all,[9-11] carbon acids are known to be slow.[12] Deviations from "normal" behavior are manifest in two ways. First, the rate constant for the proton transfer in the vicinity of $\log K_{12}' = 0$ is substantially less than the diffusion-controlled limit, and, second, the Brønsted α coefficient ($\alpha = \mathrm{d}\log k_{12}'/\mathrm{d}\log K_{12}'$) changes only gradually from 1 to 0. For ligands of this type the acid and its conjugate base differ substantially in both charge delocalization and molecular structure. The charge displacement and structural modifications which accompany the protonation are important factors contributing to the slowness of these reactions.[12,13]

The kinetics of methylmercury transfer to several carbon-donor ligands, which are known to undergo slow proton transfers, are presented. For each of the ligands investigated, the CH_3Hg^{II} transfer (eq 1) is found to be more rapid than the analogous proton-transfer (eq 2) reaction.

Experimental Section

Methylmercury hydroxide solutions were prepared and standardized as previously described.[8] Meldrum's acid,[14] 2-methyl-1,3-indandione,[15] $[Ni([14]dieneN_4)](PF_6)_2$,[16] and $[Cu([13]dienoN_4)]PF_6$[17] were synthesized by literature methods. All other ligands were either recrystallized from methanol/water or used as supplied.

The majority of the stability constants were determined spectrophotometrically by use of a Beckman Acta III spectrophotometer equipped with a thermostated cell compartment. Changes in the UV–visible spectra resulting from methylmercury complexation were used to evaluate the stability constants for the anions of Meldrum's acid, 1,3-cyclopentanedione, and 2-methyl-1,3-indandione. The stability of the methylmercury–acetylacetonate complex was determined indirectly by competition with 8-hydroxyquinoline-5-sulfonic acid as were the upper limits for the stability of the diethyl malonate and 2-acetylcyclopentanone anions. The pK_a's and stability constants for $[Ni([14]dieneN_4)]^{2+}$ and malononitrile[18] were determined potentiometrically.

The Raman spectra of the ligands and their CH_3Hg complexes were recorded on a Cary 82 Raman spectrometer. Solid samples of the complexes were prepared by mixing a 0.08 M solution of CH_3HgOH with an equivalent amount of a concentrated ligand solution.

The temperature-jump experiments were done by using a double-beam Messanlagen Studiengesellschaft temperature-jump apparatus equipped with either a 0.02- or a 0.05-μF capacitor and a high-intensity Xe source. In most cases the methylmercury complexation reactions were monitored by directly observing the absorbance due to the uncomplexed and unprotonated carbon donor ligand (L). All kinetic measurements were done at 20 °C ($I = 0.10$ ($NaClO_4$)) by using freshly prepared solutions, which had been deoxygenated by bubbling $N_2(g)$ through them. This precaution was necessary as several of the ligands used are susceptible to oxidation in solution. No additional buffers were added as the buffer capacity of the free methylmercury (CH_3Hg^+, CH_3HgOH) and/or ligand (L, HL^+) was sufficient to maintain adequate pH control. The pH of the reaction solution was measured in the temperature-jump cell with a micro glass electrode that had been standardized with solutions of known H^+ concentration.

The reciprocal relaxation time, $1/\tau$, is defined by the expression $-\mathrm{d}\delta[CH_3HgL]/\mathrm{d}t = (1/\tau)\delta[CH_3HgL]$. The reported $1/\tau$ values are the average of at least three replicates with standard deviations of 5–10%.

Results and Discussion

Equilibrium Constants. The methylmercury stability constants and ligand pK_a that have been determined are given in Table I. A number of other carbon acids were also investigated; however, the stability constants for these ligands were too small to be evaluated under the conditions used and consequently only upper limits for $\log K_{CH_3HgL}$ were obtainable. These upper limits are as follows [$\log K_{CH_3HgL}$ (pK_a)]: diethyl malonate, <8.6 (13.3); $[Cu([13]dieneN_4)]^{2+}$, $\lesssim$6.5 (9.05); 2-acetylcyclopentanone, <4.3 (7.88); 2-methyl-1,3-indandione, <4 (6.18); cyanoform, <2 (−5.1).

Raman and IR Spectra. Since most of the ligands used contain more than one potential donor atom, it is important to know at which ligand site the methylmercury coordinates. For example, with Meldrum's acid both the acidic carbon atom

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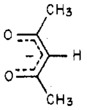
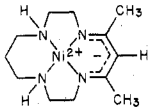
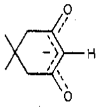
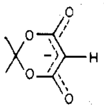
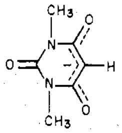
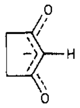
Table I. Stability Constants of the Methylmercury–Carbon Donor Complexes

protonated ligand	conjugate base (L)	pK_a	log K_{CH_3HgL}[a]
malononitrile[b]	$CH(CN)_2^-$	11.39	10.40 8.52[c]
acetylacetone		9.0[d] $(8.24)_{enol}$	5.9
$[Ni([14]dieneN_4)]^{2+}$ [b]		6.28	5.46
dimedone		5.25[e] $(5.23)_{enol}$	3.70
Meldrum's acid		4.83[f] $(2.48)_{enol}$	3.72
1,3-dimethylbarbituric acid		4.45	3.60
1,3-cyclopentanedione		4.25	2.1

[a] log K_{CH_3HgL} = log ([CH_3HgL]/[CH_3Hg] [L]); I = 0.10 ($NaClO_4$); 20 °C. [b] I = 0.10 (KNO_3); 20 °C. [c] This constant refers to the reaction $2CH_3Hg^+ + CH(CN)_2^- \rightleftarrows (CH_3Hg)_2C(CN)_2 + H^+$. [d] Reference 12. [e] G. Schwarzenbach and E. Felder, *Helv. Chim. Acta,* **27,** 1710 (1944). [f] Reference 19.

and the carbonyl oxygen atom are potentially susceptible to methylmercuration. In fact, Meldrum's acid itself is known to exist in both the keto (protonated C) and enol (protonated O) tautomeric forms,[19] although the keto tautomer is by far the predominant species in aqueous solution. Similarly, in deuteriochloroform at −60 °C the enol and keto tautomers of the methylmercury–acetylacetonate complex are present in approximately equal proportions.[20]

Because of its intensity, the symmetric methyl C–Hg stretching vibration is one of the most easily identified bands in the Raman spectrum of methylmercury complexes. This vibration is sensitive to the trans donor atom and has previously been used to distinguish between O- and S-coordination.[21] From the data presented in Table II it can be seen that it is also possible to distinguish between C- and O-coordination. For oxygen donors the methyl–Hg vibration occurs between 580 and 565 cm^{-1}, while for C-atom donors it lies between 540 and 565 cm^{-1}. The site of methylmercuration has been assigned on this basis for the ligands listed in Table II.

Table II. Raman Frequencies of the Symmetric Methyl C–Hg Vibration in the Methylmercury Complexes

complex	$\bar{\nu}_{CH_3-Hg}$, cm^{-1}	donor atom
CH_3Hg meldrumate[b]	550	C
$CH_3HgCH(CN)_2$ [c]	545[a]	C
$CH_3HgCH(CN)(SO_2C_6H_5)$[c]	545 (540)[a]	C
CH_3Hg dimethylbarbiturate[c]	543	C
CH_3Hg dimedonate[c]	540	C
CH_3Hg barbiturate[c]	570	O/N
CH_3HgCH_3 [d]	550	C
CH_3HgCN[e]	564	C
$CH_3HgOH_2^+$[f]	570	O
CH_3HgOH[g]	577	O
CH_3HgONO_2 [f]	566	O
$CH_3HgOSO_3^-$[h]	566	O
CH_3HgNH_3 [i]	565	N

[a] IR, CsBr pellet. [b] Aqueous solution; 0.04 M, pH 4.7. [c] Solid sample. [d] K. Brodersen, *Chem. Ber.*, 90, 2703 (1957). [e] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 62, 1423 (1966). [f] P. L. Goggin and L. A. Woodward, *ibid.*, 58, 1495 (1962). [g] P. L. Goggin and L. A. Woodward, *ibid.*, 56, 1591 (1960). [h] J. H. R. Charke and L. A. Woodward, *ibid.*, 64, 1041 (1968). [i] W. Beitelschmidt, Dissertation, Friedrich-Alexander-Universität, Erlangen-Nürnberg, 1972.

Transfer of CH_3Hg^+ from H_2O to Carbon-Donor Ligands. A. Meldrum's Acid. When the course of the reaction between CH_3Hg^+ and Meldrum's acid anion is followed directly at 260 nm on a temperature-jump apparatus, two relaxations are observable. The slower process exhibits relaxation time in the vicinity of 30 ms, which is in good agreement with that expected for the slow ligand-protonation reaction.[19] Relaxation times of 10–35 μs (Table III) are observed for the faster process. This faster relaxation corresponds to the methylmercuration reaction (eq 3), where E$^-$ is the enolate anion of

$$CH_3Hg^+ + E^- \underset{}{\overset{k_f^{MA}}{\rightleftarrows}} CH_3HgK \qquad (3)$$

Meldrum's acid and K is the keto form (C-bound) of the ligand. Under the conditions used, the protonation reactions (4) and (5) are rapid compared to reaction 3. The reciprocal

$$CH_3HgOH + H^+ \rightleftarrows CH_3Hg^+ \qquad (4)$$

$$E^- + H^+ \rightleftarrows EH \qquad (5)$$

relaxation time, $1/\tau$, for reaction 3 is given by eq 6. (Charges

$$1/\tau = k_f^{MA}([CH_3Hg]F_1 + [E]F_2 + 1/K_{CH_3HgK}) = k_f^{MA}f_1 \qquad (6)$$

Table III. Concentration Dependence of the Relaxation Time for the Reaction of the Methylmercury Cation with Meldrum's Acid Anion[a]

pH	$10^4 \times$ [HL]$_t$, M	$10^4 \times$ [CH$_3$Hg]$_t$, M	$10^4 \times$ f_1,[b] M	$10^{-4} \times$ $(1/\tau)$, s^{-1}	$10^{-8}k_f^{MA}$, M^{-1} s^{-1}
4.57	1.01	0.98	2.62	3.1	1.18
4.90	1.02	1.23	2.68	2.9	1.08
4.72	1.16	1.43	2.84	2.9	1.02
4.78	1.16	1.97	3.01	3.5	1.16
4.89	1.02	2.46	3.07	3.4	1.10
4.56	1.01	1.97	3.10	3.0	0.97
4.80	1.16	2.46	3.17	3.2	1.01
4.60	1.02	2.46	3.30	3.1	0.94
4.70	1.01	2.98	3.41	3.0	0.88
4.50	4.16	2.08	3.68	4.0	1.09
4.40	1.01	2.95	3.76	3.2	0.85
4.60	1.01	4.16	4.07	3.3	0.81
4.71	0.50	4.92	4.10	3.3	0.80
4.90	1.02	6.15	4.10	3.5	0.85
4.84	1.01	6.24	4.32	5.0	1.16
4.58	4.16	4.16	4.52	4.2	0.93
4.83	1.01	8.23	5.05	5.4	1.07
4.72	4.16	6.24	5.12	5.2	1.02
4.82	1.01	10.4	5.80	5.8	1.00
4.82	1.05	10.4	6.56	6.6	1.01
4.56	4.16	10.4	7.05	7.8	1.11
4.56	4.16	14.6	8.87	8.9	1.00
4.67	4.16	20.8	10.7	11.5	1.07
				av	1.0 ± 0.1

[a] $I = 0.10$ (NaClO$_4$); 20 °C. [b] See eq 6.

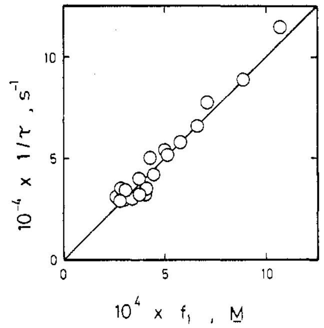


Figure 1. Concentration dependence for the reaction of CH_3Hg^+ with the conjugate base of Meldrum's acid.

are omitted in concentration expressions.) The correction factors F_1 and F_2 account for the rapid preequilibrium reactions (4) and (5) and are F_1 = ([H]a + [CH$_3$HgOH] + [EH])/A and F_2 = ([H]b + [CH$_3$HgOH] + [EH])/A, where a = 1 + [CH$_3$HgOH]/[CH$_3$Hg], b = 1 + [EH]/[E], and A = [H]ab + [CH$_3$HgOH]b + [EH]a. A linear least-squares analysis of the data plotted in Figure 1 yields a value of (1.0 ± 0.1) × 10^8 M^{-1} s^{-1} for k_f^{MA}.

Two tautomeric forms (enol and keto) of the CH$_3$Hg–Meldrum's acid anion complex may exist; however, neither the Raman spectrum nor the kinetics indicates such a tautomerization. From the kinetic results it is possible to place an upper limit on the stability of the enol tautomer with log $K_{CH_3HgE} < 2.7$. If this were not the case, significant curvature would have been observed in the kinetic plot (Figure 1), since the value of k_f^{MA} would depend on the concentration function (viz., $k_f^{MA} = k_f'/(1 + K_{CH_3HgE}f_1)$). Thus for Meldrum's acid the ratio of tautomeric forms, [CH$_3$HgK]/[CH$_3$HgE], is greater than 10. For the proton the analogous ratio, [HK]/[EH], is 220.[19]

Table IV. Concentration Dependence of the Relaxation Time for the Reaction of the Methylmercury Cation with [Ni([14]dienoN$_4$)]$^+$, L[a]

pH	$10^4 \times$ [CH$_3$Hg]$_t$, M	$10^4 \times$ [L]$_t$, M	$10^5 \times$ f_2,[b] M	$10^{-4} \times$ $(1/\tau)$, s^{-1}	$10^{-8}k_f^{L}$,[b] M^{-1} s^{-1}
5.81	2.00	2.17	3.02[c]	1.9	6.30
5.32	2.00	2.17	3.30[c]	2.2	6.66
5.39	2.08	4.22	4.15	2.5	6.02
5.80	4.16	2.11	4.22	2.3	5.45
5.47	4.16	2.11	4.89	3.2	6.55
5.42	4.00	4.34	5.06[c]	3.5	6.91
5.74	4.00	4.34	5.23[c]	2.9	5.55
5.76	4.00	4.34	5.27[c]	3.1	5.89
5.39	4.16	4.22	5.39	3.5	6.49
5.24	4.00	4.34	5.54[c]	3.7	6.68
5.75	4.16	4.22	6.18	3.0	4.85
5.04	4.00	4.90	6.51	4.2	6.45
5.43	6.00	7.35	7.19	4.3	5.98
5.57	6.00	7.35	7.79	4.1	5.27
				av	6.1 ± 0.6

[a] $I = 0.10$ (NaClO$_4$); 20 °C. [b] $k_f^L = (1/\tau)/f_2$; see eq 8. [c] pH indicator: [chlorophenol red]$_t$ = 2.0 × 10^{-5} M.

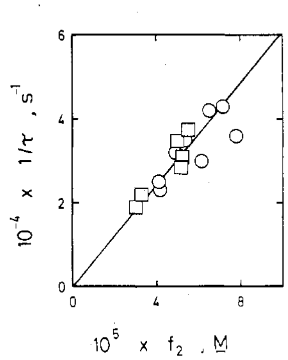


Figure 2. Concentration dependence for the reaction of CH_3Hg^+ with [Ni([14]dienoN$_4$)]$^+$. pH indicator was used in solutions indicated by □.

B. [Ni([14]dieneN$_4$)]$^{2+}$. The reaction of CH_3Hg^+ with the base [Ni([14]dienoN$_4$)]$^+$, L, was monitored by directly observing the absorbance due to the uncomplexed ligand at 357 nm (ϵ 7250 M^{-1} cm^{-1}) as well as the absorbance in the presence of the pH indicator chlorophenol red (pK_a = 6.00). After the temperature jump, two relaxations were observed. The longer relaxation time corresponds to the slow protonation of L,[22] while the faster reaction corresponds to the methylmercuration reaction (7). The reciprocal relaxation time is given by eq

$$CH_3Hg^+ + L \underset{}{\overset{k_f^L}{\rightleftharpoons}} CH_3HgL^+ \qquad (7)$$

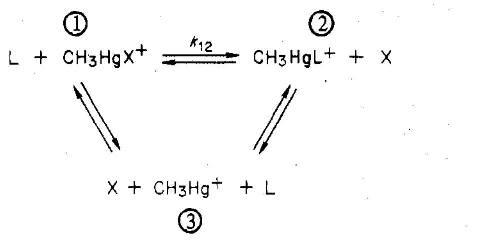
8, where F_3 = ([H] + [CH$_3$HgOH] + c)/([H]a + [CH$_3$HgOH] + ac) and $c = K_{HIn}[H][In]_t/(1 + K_{HIn}[H])^2$.

$$1/\tau = k_f^L([CH_3Hg] + [L]F_3 + 1/K_{CH_3HgL}) = k_f^L f_2 \qquad (8)$$

A linear plot of the data (Figure 2, Table IV) yields a value of (6.1 ± 0.6) × 10^8 M^{-1} s^{-1} for k_f^L. As can be seen in Figure 2, this result is not influenced by a pH indicator.

C. Other Ligands. Solutions of CH$_3$Hg^{II} containing dimedone and 1,3-dimethylbarbituric acid, respectively, like those with Meldrum's acid and [Ni([14]dieneN$_4$)]$^{2+}$, show two relaxation times after the temperature jump. However, because of the relatively small reaction amplitudes and the rapidity ($\tau < 10$ μs) of the reactions, only a lower limit for k_f could be determined. In both cases k_f is greater than 10^8 M^{-1} s^{-1}.

Transfer of CH$_3$Hg^{II} from Nitrogen Bases to [Ni([14]dienoN$_4$)]$^+$. The methylmercury-transfer reaction between nitrogen base ligands, X, and [Ni([14]dienoN$_4$)]$^+$, L, proceeds by two pathways (eq 9). In addition to the direct CH$_3$Hg^{II} transfer (1–2), an indirect pathway, (1–3–2), which proceeds via the solvated CH_3Hg^+ cation, is also present. It was necessary to include this indirect reaction pathway in order



(9)

to fit the observed concentration dependence for the shorter relaxation time, which will be discussed below. Again a second relaxation time could be detected which corresponds to the protonation of L.

A. 3-Picoline. When X is 3-pic, the methylmercury cation, CH_3Hg^+, can be treated as a steady-state species and the observed reciprocal relaxation time, $1/\tau$, is given by eq 10.

$$1/\tau = k_o([CH_3HgX] + [L]F_4 + ([CH_3HgL]F_5 + [X])/K_{12}) = k_of_3 \quad (10)$$

The correction factors F_4 and F_5, which account for the rapid protonations of CH_3HgOH and X, are $F_4 = ([H]d + [CH_3HgOH]d + [HX])/B$ and $F_5 = ([H] + [CH_3HgOH] + [HX])/B$, where $B = [H]d + [CH_3HgOH] + [HX]$ and $d = 1 + [HX]/[X]$. The observed rate constant, k_o, contains contributions from both the direct reaction ((1–2) in eq 9) and the indirect (1–3–2) solvent pathway and is given by eq 11.

$$k_o = k_{12} + \frac{k_{13}k_{32}}{k_{31}[X] + k_{32}[L]} \quad (11)$$

The magnitudes of $k_{31}[X]$ and $k_{32}[L]$ are similar. A nonlinear least-squares regression analysis of the data (Table V) yields values of $(4.2 \pm 0.4) \times 10^7\ M^{-1}\ s^{-1}$ and $(3.3 \pm 0.7) \times 10^8\ M^{-1}\ s^{-1}$ for the rate constants k_{12} and k_{31}, respectively. In this analysis, the value of k_{32} was not varied as it had been independently determined to be $6.1 \times 10^8\ M^{-1}\ s^{-1}$. The equilibrium relation, $k_{13} = k_{31}/K_{31}$, can be used to calculate $k_{13} = 6.1 \times 10^3\ s^{-1}$.

B. Ammonia. When X is ammonia, the NH_3 species is the lowest concentration species in solution and can be treated as being present in steady-state concentrations. The observed relaxation time is then given by eq 12, where $F_6 = ([H] + [CH_3HgOH] + [HX] + c)/([H]a + [CH_3HgOH] + [HX] + ac)$ and k_o is defined by eq 13. Under all conditions used (Table VI), $k_{12}[CH_3HgX]$ is much less than $k_{32}[CH_3Hg]$, permitting the simplification of eq 13 to the linear form given in eq 14. The intercept of the linear plot of eq 14 (Figure 3) yields a value of $(8.2 \pm 0.8) \times 10^8\ M^{-1}\ s^{-1}$ for k_{32}, which is in good agreement with the previously determined value of 6×10^8. From the slope and intercept of Figure 3 and by use of $k_{31} = (1.3 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$,[23] k_{21} is calculated to be $(1.2 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$. The equilibrium relation $k_{12} = k_{21}K_{12}$ then gives $k_{12} = (8.7 \pm 2.2) \times 10^5\ M^{-1}\ s^{-1}$.

$$1/\tau = k_o([CH_3Hg] + [L]F_6 + 1/K_{32}) = k_of_4 \quad (12)$$

$$k_o = \frac{k_{31}(k_{12}[CH_3HgX] + k_{32}[CH_3Hg])}{k_{31}[CH_3Hg] + k_{21}[CH_3HgL]} \quad (13)$$

$$\frac{1}{k_o} = \frac{1}{k_{32}} + \frac{k_{21}}{k_{31}k_{32}}\frac{[CH_3HgL]}{[CH_3Hg]} \quad (14)$$

Discussion

Linear correlations between the methylmercury stability constant, $\log K_{CH_3HgL}$, and the ligand pK_a have previously been demonstrated for ligands containing P-, S-, N-, and O-donor atoms.[3,4,7] The analogous correlation ($\log K_{CH_3HgL} = 0.8\ pK_a$) for carbon-donor ligands (Figure 4) is not as well-defined. This is attributed to the diversity of C ligands used. While Meldrum's acid exists primarily in the keto tautomeric form, dimedone is present in solution predominantly as the enol tautomer. In addition, the solvation changes accompanying complex formation are expected to vary considerably from ligand to ligand. As indicated above the value of $\log K_{CH_3HgL}$

Table V. Observed and Calculated Second-Order Rate Constants for the Transfer of CH_3Hg^{II} from 3-Picoline, X, to $[Ni([14]dienoN_4)]^+$, L[a]

pH	$10^4 \times [CH_3Hg]_t$, M	$10^4 \times [L]_t$, M	$10^4 \times [X]_t$, M	$10^{-4} \times (1/\tau)$, s^{-1}	$10^{-7} \times k_o$,[b] $M^{-1}\ s^{-1}$	$10^{-7} \times k_o^{calcd}$, $M^{-1}\ s^{-1}$
5.94	6.00	4.90	20.4	3.1	5.1	5.2
5.73	4.00	4.90	20.4	2.3	5.0	5.4
5.54	6.00	4.90	20.4	4.1	7.9	6.0
5.47	4.00	4.90	20.4	2.8	7.1	6.0
5.74	6.00	4.90	10.2	2.65	6.7	6.7
5.65	4.00	4.90	10.2	2.1	6.8	6.8
5.43	4.00	4.90	10.2	2.4	8.6	7.9
5.92	2.04	4.56	4.08	1.15	5.3	7.1
5.84	4.09	2.28	4.08	2.1	11.2	9.6
5.50	2.04	4.56	4.08	1.5	10.2	9.8
5.49	4.09	2.28	4.08	2.3	13.3	13.6
5.62	4.09	4.56	2.04	2.3	12.9	12.2
5.62	4.09	2.28	2.04	2.4	18.8	16.9
5.49	4.09	4.56	2.04	2.9	17.4	14.3
5.42	4.09	2.28	2.04	2.4	19.7	22.3

[a] $I = 0.10$ ($NaClO_4$); 20 °C. [b] $k_o = (1/\tau)/f_3$; see eq 10.

Table VI. Concentration Dependence of the Relaxation Time for the Transfer of CH_3Hg^{II} from NH_3 to $[Ni([14]dienoN_4)]^+$, L[a]

pH	$10^4 \times [CH_3Hg]_t$, M	$10^4 \times [L]_t$, M	$10^4 \times [NH_3]_t$, M	$10^{-4} \times (1/\tau)$, s^{-1}	$10^9 \times (1/k_o)$, M s	$[CH_3HgL]/[CH_3Hg]$
5.31	2.04	2.08	4.72	2.0	1.70	3.89
5.51	4.09	2.08	4.72	2.3	1.90	4.14
5.09	6.00	4.26	47.2	3.4	1.61	4.61
5.03	4.00	4.26	47.2	3.15	2.09	4.71
5.45	4.09	2.15	47.2	1.6	2.17	5.46
5.37	4.09	4.16	47.2	2.7	1.98	7.23
5.35	4.00	4.30	23.6	2.6	1.92[b]	8.51
5.48	4.09	4.16	2.36	2.9	1.86	8.77
5.35	4.09	4.30	47.2	2.4	2.03	9.35
5.32	2.04	4.30	47.2	1.7	2.68	10.3
6.02	4.09	2.08	4.72	1.9	2.60	11.1
5.52	4.09	4.30	23.6	2.7	2.11	12.0
5.49	4.00	4.30	47.2	2.3	2.43[b]	12.6
5.81	4.09	4.16	4.72	2.4	2.96	17.2
5.84	4.09	4.16	2.36	2.6	2.75	17.6
5.78	4.00	4.30	23.6	2.4	3.21[b]	20.0
5.90	4.09	4.30	23.6	2.2	4.26	24.7
5.97	4.00	4.30	47.2	2.3	4.82[b]	31.0

[a] $I = 0.10$ ($NaClO_4$); 20 °C. [b] pH indicator: [chlorophenol red] = 2.0×10^{-5} M.

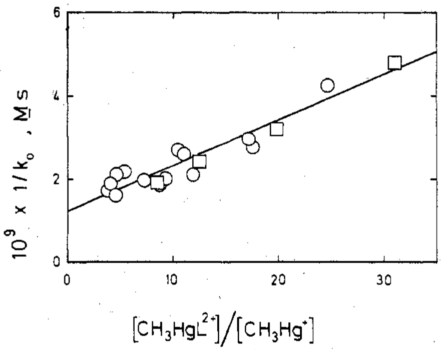


Figure 3. Resolution of the data for the transfer of CH_3Hg^+ from NH_3 to $[Ni([14]dienoN_4)]^+$. Solutions containing pH indicator are indicated by □.

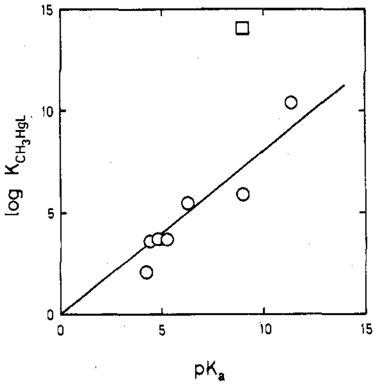


Figure 4. Correlation between the methylmercury stability constants and the ligand pK_a. □ is for CN^-.[1]

is normally less than that of the ligand pK_a. The only exception to this observation is provided by the cyanide ion (log $K_{CH_3HgCN} = 14.1$, $pK_a = 9.0$).[1] The CN^- ion is well-known to be a rather soft pseudohalide which is expected to behave quite differently from the other carbon-donor ligands.

The CH_3Hg–Meldrum's acid complex exists in solution primarily as the C-bound (keto) tautomer, CH_3HgK, and the formation rate constant, k_f^{MA}, measures the rate at which this complex is formed. However, two pathways are possible for the reaction. The first of these (eq 3) is the direct reaction of the methylmercury cation with the carbon atom of the ligand, and it is the rate constant for this reaction that must be considered when the methylmercury cation and proton reactivities are compared. An alternate indirect route proceeds through the initial formation of an oxygen-bound (enol) tautomer (eq 15) followed by an intramolecular rearrangement

$$CH_3Hg^+ + E^- \rightleftarrows CH_3HgE \qquad (15)$$

(eq 16). Intramolecular enol–keto rearrangements have been

$$CH_3HgE \rightleftarrows CH_3HgK \qquad (16)$$

observed for several Hg(II) β-diketonate complexes in acetone and $CDCl_3$ solution and are much slower than the reactions observed here.[24]

A decision as to the relative importance of the direct (eq 3) and indirect (eq 15 and 16) reaction pathways cannot be made solely on the basis of the CH_3Hg–Meldrum's acid results. The $[Ni([14]dienoN_4)]^+$ ligand, unlike the anion of Meldrum's acid, contains only one potential ligating atom (the basic C atom) and thus only a direct methylmercuration reaction pathway is possible. k_f for this ligand is 200 times larger than the protonation rate constant, indicating that CH_3Hg^+ can react directly and more rapidly than hydronium ion with the carbon-donor ligands. Further, it may be concluded that the rapidity of the CH_3Hg–Meldrum's acid reaction can be accounted for solely by the presence of the direct (eq 3) reaction pathway.

Table VII lists the rate constants determined for the methylmercury transfers to carbon-donor ligands and compares them to the rate constants for the analogous proton-transfer reactions. In each instance the methylmercury transfer is more rapid than the proton transfer and in one case ($[Ni([14]dienoN_4)]^+$, 3-pic) it is more than *4 orders of magnitude* faster.

Reaction rate–equilibria correlations of atom-transfer reactions in general, and proton-transfer reactions in particular, have been widely discussed.[25-28] Marcus' treatment[25] of the atom-transfer reaction (17), in which the transfer step and not

$$L + MX \overset{k_{12}}{\rightleftarrows} LM + X \qquad (17)$$

diffusion is rate determining, relates the free energy of reaction within the reaction complex, $\Delta F°_R'$ ($=\Delta F° - W^r + W^p$), to the free energy of activation, ΔF^*, by eq 18–20. The work

$$\Delta F^* = W^r + \lambda(1 + \Delta F°_R'/\lambda)^2/4 \qquad |\Delta F°_R'| < \lambda \qquad (18)$$

$$\Delta F^* = W^r \qquad \Delta F°_R' < -\lambda \qquad (19)$$

$$\Delta F^* = W^r + \Delta F°_R' \qquad \Delta F°_R' > \lambda \qquad (20)$$

required to bring the reactants (or products) together to form the reaction complex is W^r (or W^p). This term also includes the entropy of localization, the free energy of solvation, and the energies due to steric and statistical factors which are required in order to form the reaction complex. W^r is independent of changes in the stability (log K_{MX}) of the MX molecule for any reasonably homologous series of ligands X and determines the maximum rate of atom transfer for strongly exergonic (log $K_{12} >> 0$) reactions. The intrinsic reorganizational energy barrier, $\lambda/4$, is associated with the need for electronic redistribution and structural (bond length) alterations during the course of the atom transfer.[26,27] The value of λ determines the broadness of the Brønsted plot. That is, the larger λ is, the more gradually the Brønsted slope, α (=d log k_{12}/d log K_{12}), changes from 1 to 0.

Marcus has pointed out that changes in the extent of conjugation within a ligand can affect the value of λ.[25] Highly conjugated ligands which experience large amounts of electronic redistribution and bond reorganization during the atom transfer are characterized by large values of λ, while λ is small for those ligands which do not require significant amounts of electronic and structural reorganization. That this is the case can be seen by comparing the Brønsted plots obtained for the proton-transfer reactions of the ketonic,[12,19,26,29] macrocyclic,[22] and *p*-nitrobenzyl cyanide[13] carbon-acid ligands to those obtained for nitrile activated C acids.[9,10]

The magnitude of λ will be affected not only by the nature of the ligand, L, but also by the nature of the atom being transferred. The manner in which λ is influenced by the transferred atom, M, can be visualized by considering the following. For some ligand L, which experiences a large degree of electronic and structural reorganization during the atom transfer as a result of changes in conjugation, λ is expected to be large if the transferred atom, M, is the proton. If M is chosen so that it interacts more favorably with the delocalized electron density (π orbitals) of L than does the proton, the resulting bridged transition-state complex will be more stable than is the case when M is H^+, and consequently the reorganizational energy barrier, $\lambda/4$, will be smaller. This can be restated as follows. For atom-transfer reactions between two ligands L and X, the magnitude of the reorganizational energy barrier, $\lambda/4$, will decrease as the "bridging ability" of the transferred atom increases. This can be demonstrated by comparing the Brønsted plots obtained when the atom[30] being transferred is H^+ or CH_3Hg^{II}. Methylmercury(II) is a better bridging atom than is the proton, and thus, if the preceding argument is correct, λ will be smaller for the CH_3Hg^{II} transfers than for the H^+ transfers.

Figure 5 compares the Brønsted plots obtained for the H^+ and CH_3Hg^{II} transfers to the $[Ni([14]dienoN_4)]^+$ ligand. The reorganizational energy is large ($\lambda/4 = 88$ kJ/mol) for the transfer of a proton to this ligand, and the Brønsted plot is characteristically broad.[22] The plot for the CH_3Hg^+ transfer (Figure 5, line A) exhibits a much sharper transition from $\alpha = 1$ to $\alpha = 0$, and the solid line A in Figure 5 is calculated from eq 18 by using $\lambda/4 = 9$ kJ/mol and $W^r = W^p = 22$ kJ/mol. As indicated earlier, eq 18–20 apply to reactions in which the transfer step and not diffusion is rate-determining.[25,28] For the CH_3Hg^{II} transfers under consideration, the diffusion step, k_{diff}, is expected to make some contribution to the experimentally observed transfer rate constant, k_{12}. In such a case, the actual transfer rate constant, k_{12}^T, can be calculated

Table VII. Comparison of the Second-Order Rate Constants, M^{-1} s^{-1}, for the Transfer of Methylmercury(II) and the Proton from X to Carbon-Donor Ligands

ligands			log k_{12}		
HL	X^a	log $K_{12}{}^a$	$H_3O^{+\,b}$	CH_3-HgX^a	$HX'^{\,c}$
$[Ni[14]dieneN_4]^{2+}$	H_2O	7.20	6.3^d	8.8	6.3
	3-pic	0.77	...	7.6	3.1
	NH_3	−2.14	...	5.9	1.6
Meldrum's acid	H_2O	5.46	5.7^e	8.0	
dimedone	H_2O	5.4		>8	
1,3-dimethyl-barbituric acid	H_2O	5.3	(5–6)	>8	

[a] For the reaction $L + CH_3HgX^+ \rightarrow CH_3HgL^+ + X$ (k_{12}). [b] For the reaction $L + H_3O^+ \rightarrow HL^+ + H_2O$. [c] Estimated (line B in Figure 5) for the reaction $L + HX'^+ \rightarrow HL^+ + X'$, with X′ such that $[CH_3HgL][X]/[CH_3HgX][L] = [HL][X']/[HX'][L]$. [d] Reference 22. [e] Reference 19.

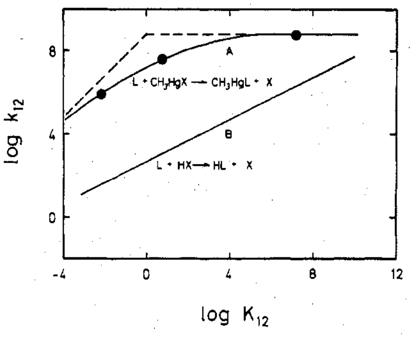


Figure 5. Brønsted plot for the atom transfers to the $[Ni([14]dienoN_4)]^+$ ligand: A, CH_3Hg^+ transfer; B, H^+ transfer.[22]

from the expression $1/k_{12}{}^T = 1/k_{12} - 1/k_{diff} - 1/(K_{12}ak_{diff})$, where a is the ratio of the diffusion rate constants for the reverse and forward directions. When $k_{diff} = 1 \times 10^9$ M^{-1} s^{-1} and $a = 1$, the corrected values of W^r and $\lambda/4$ are 20 kJ/mol and 11 kJ/mol, respectively. Thus, the contribution from the diffusion step does not cause a large error in the calculated values of W^r and $\lambda/4$ even when it is ignored. Because of the limited amount of data, the accuracy of the W^r and $\lambda/4$ values is not high. As an extreme case, W^r could be as small as 0 and $\lambda/4$ as large as 30 kJ/mol. In any case $\lambda/4$ is much smaller when the atom being transferred is CH_3Hg^{II} rather than the proton. This decrease confirms the proposal that the value of $\lambda/4$ will be influenced by the identity of the transferred atom and demonstrates that, at least for the reaction system considered here, this influence can be very large.

The proposal that the identity of the transferred atom can significantly alter the value of $\lambda/4$, and thus the broadness of a Brønsted plot leads to several interesting consequences: (1) The transfer reactions of other ligand systems are also expected to be influenced by the identity of the transferred atom, M^+, as the $[Ni([14]dienoN_4)]^+$ ligand is not unique in this respect. Qualitatively, the results obtained with the anions of Meldrum's acid and 1,3-dimethylbarbituric acid appear to be similarly affected. That is, k_{12} is larger when M^+ is CH_3Hg^+ rather than H^+. In addition, preliminary results for the reactions of CH_3Hg^{II} with S donors[31] also appear to be in agreement. (2) For $[Ni([14]dienoN_4)]^+$ as well as other ligands, which are characterized by large $\lambda/4$'s when the atom, M^+, being transferred is H^+, it should be possible to find a series of M^+ (e.g., $M^+ = H^+, Ag^+, CH_3Hg^+$) such that a series of Brønsted plots of varying broadness can be obtained. The broadness (determined by the $\lambda/4$ values) of these plots will depend on the "bridging ability" of M^+ and ought to vary in at least a qualitatively predictable manner. (3) A final consequence of the present results is that CH_3Hg^+ can be expected to more efficiently catalyze reactions which involve the rearrangement of multiple (double and triple) bonds than does the proton. An example of such a case has recently been observed in the dissociation reactions of the bis(methylmercury) malononitrile complex.[18]

Conclusions

In aqueous solution carbon-donor ligands show a thermodynamic preference for protonation over methylmercuration. Kinetically the opposite is true, with methylmercuration being distinctly more rapid than protonation. A comparison of the Brønsted plots for CH_3Hg^{II} transfer and H^+ transfer shows that the methylmercury(II)-transfer reactions can be more than *4 orders of magnitude* faster than the proton-transfer reactions and that the reorganizational energy barrier, $\lambda/4$, is much smaller when CH_3Hg^{II} rather than when the proton is the atom being transferred. The reduction in λ is attributed to the superior bridging ability of methylmercury(II).

Acknowledgment. This investigation was supported by grants from the Swiss National Science Foundation (Project Nos. 2.332–0.75 and 2.818.077).

Registry No. Methylmercury propanedinitrile, 70714-03-3; methylmercury acetylacetonate, 59557-23-2; $\{CH_3Hg[Ni([14]dienoN_4)]\}^{2+}$, 70728-84-6; methylmercury dimedonate, 70714-04-4; methylmercury meldrumate, 70714-05-5; methylmercury 1,3-dimethylbarbiturate, 70714-06-6; methylmercury 1,3-cyclopentanedionate, 70714-07-7; methylmercury diethylmalonate, 70714-08-8; $\{CH_3Hg[Cu([13]dienoN_4)]\}^{2+}$, 70775-73-4; methylmercury 2-acetylcyclopentanonate, 70714-09-9; methylmercury 2-methyl-1,3-indandionate, 70714-10-2; methylmercury cyanoformate, 70714-11-3; malononitrile, 58821-77-5; $[Ni([14]dieneN_4)]^{2+}$, 46754-95-4; 1,3-dimethylbarbituric acid, 769-42-6; 1,3-cyclopentanedione, 3859-41-4; diethyl malonate, 105-53-3; 2-acetylcyclopentanone, 1670-46-8; 2-methyl-1,3-indandione, 876-83-5; $[Cu([13]dieneN_4)]^{2+}$, 46472-97-3; cyanoform, 454-50-2; CH_3H_9-$CH(CN)(SO_2C_6H_5)$, 70714-12-4; methylmercury barbiturate, 70714-13-5; CH_3Hg^+, 22967-92-6; $CH_3Hg(3\text{-pic})^+$, 56665-04-4; $CH_3Hg(NH_3)^+$, 43408-29-3; $CH_3Hg(H_2O)^+$, 18042-02-9.

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