solvent association at the ammine groups, which is more pronounced when the metal atom has a higher formal charge. The ability of these solutes to act as acceptors leads to solvent–solute and anion–solute effects that are not predicted by an assumption of the medium as a dielectric continuum.

The evidence obtained for preferential solvent-sorting and ion-pairing interactions points out that care must be exercised in interpreting the outer-sphere electron-transfer kinetics involving metal–ammine complexes.

Finally, specific solvent donor–solute acceptor interactions should affect the redox potentials and spectral transition energies in metal complexes involving primary or secondary amines, H_2O, imidazole, and other hydrogen-bond donor ligands, all of which can, in principle, hydrogen bond to solvents.

Acknowledgments are made to the Army Research Office—Durham under Grant No. DAAG29-79-C-0044 for support of this research.

Registry No. $[Ru(bpy)(NH_3)_4](PF_6)_2$, 74887-15-3; $[Ru(NH_3)_5(py)](PF_6)_2$, 72905-29-4; $[Ru(NH_3)_5$(4-CN-*N*-Mepyd)]$(PF_6)_3$, 79447-33-9; *trans*-[(py)$Ru(NH_3)_4$(4-CN-*N*-Mepyd)]$(PF_6)_3$, 83477-07-0; *trans*-[(3-Cl-py)$Ru(NH_3)_4$(4-CN-*N*-Mepyd)]$(PF_6)_3$, 83477-09-2; *trans*-[(3,5-Cl_2py)$Ru(NH_3)_4$(4-CN-*N*-Mepyd)]$(PF_6)_3$, 83477-11-6; $[Ru(NH_3)_5$(*N*-Me-4,4′-bpy)]$(PF_6)_3$, 79447-35-1; *trans*-[(py)$Ru(NH_3)_4$(*N*-Me-4,4′-bpy)]$(PF_6)_3$, 83477-13-8; *trans*-[(3-Cl-py)$Ru(NH_3)_4$(*N*-Me-4,4′-bpy)]$(PF_6)_3$, 83477-15-0; *trans*-[(3,5-Cl_2py)$Ru(NH_3)_4$(*N*-Me-4,4′-bpy)]$(PF_6)_3$, 83477-17-2; $[Ru(NH_3)_5(dmabn)](PF_6)_2$, 83477-19-4; $[Ru(NH_3)_5(dmabn)]Cl_3$, 83477-20-7; $[Ru(NH_3)_5(dmapy)](PF_6)_2$, 83477-22-9; $[Ru(NH_3)_5(dmapy)]Cl_3$, 79447-36-2; NM, 75-52-5; NB, 98-95-3; BN, 100-47-0; AN, 75-05-8; PC, 25511-85-7; AC, 67-64-1; NMF, 123-39-7; TBP, 126-73-8; DMF, 68-12-2; DMA, 127-19-5; Me_2SO, 67-68-5; HMPA, 680-31-9.

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Investigation of Reduction and Exchange Reactions of Mercury(II) Phosphine Complexes at Mercury Electrodes in Dichloromethane

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The electrochemical reduction at mercury electrodes of a series of $[HgP_2](ClO_4)_2$ complexes (P = phosphine) has been investigated by using dc and differential-pulse polarography. Data from mercury-199 and phosphorus-31 NMR data are used in conjunction with electrochemical results to aid the interpretation of the electrode processes. In dichloromethane, the charge-transfer step is of unity order. Thus, the polarographic half-wave potential, $E_{1/2}$, is independent of the concentration of either $[HgP_2]^{2+}$ or P, and despite evidence for formation of $[HgP_n]^{2+}$ (n = 2–4) complexes from NMR data, these complexes are not observed at the electrode surface. Instead, the electrochemical data appear as the superimposition of the electrode processes for reduction of the $[HgP_2]^{2+}$ complex and oxidation of the ligand in the presence of mercury to produce $[HgP_2]^{2+}$. A reaction scheme consistent with the observed characteristics of the electrode process is

$$[HgP_2]^{2+} + Hg \rightleftharpoons 2[HgP]^+ \qquad (1)$$

$$2[HgP]^+ + 2e^- \rightleftharpoons 2Hg + 2P \qquad (2)$$

to give an overall reaction

$$[HgP_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P \qquad (3)$$

The large substituent effect observed with different phosphine ligands, and the unusual nature of the electrode process, implies that the presence of mercury(I), or elemental mercury, can catalyze exchange reactions at the electrode surface and modify others. Thus, polarograms for reduction of $[HgP_2]^{2+}$, of $[HgP'_2]^{2+}$ ($P \neq P'$), or of $[HgP_2]^{2+}$ and 2P′ may be substantially different when both phosphines are present simultaneously compared with polarograms obtained from individual solutions. Electrochemical studies on mixtures of compounds show that the following reactions and probably other second-order exchange reactions are significant at mercury electrodes ($E_{1/2}[HgP'_2]^{2+}$ more negative than $E_{1/2}[HgP_2]^{2+}$):

$$[HgP_2]^{2+} + [HgP'_2]^{2+} \rightleftharpoons 2[HgPP']^{2+} \qquad (4)$$

$$[HgP_2]^{2+} + P' \rightleftharpoons [HgPP']^{2+} + P \qquad (5)$$

$$[HgPP']^{2+} + P' \rightleftharpoons [HgP'_2]^{2+} + P \qquad (6)$$

NMR data confirm the existence of complex exchange reactions, although precipitation of complexes from some mixtures, and the ability of elemental mercury to modify reactions, implies that considerable care is required in the interpretation of the NMR data.

Introduction

Mercury compounds exhibit a wide range of coordination numbers and stereochemistries. Mercury has one isotope, ^{199}Hg, of nuclear spin $^1/_2$ and reasonable abundance, which, with the advent of commercially available Fourier transform NMR spectrometers, allows solutions in the 0.1 M and higher concentration range to be studied readily by mercury NMR to provide considerable information on the nature of species in solution.[5]

Mercury-199 NMR studies on phosphine complexes of mercury(II) have been hampered by the inadequate solubility of many of the complexes, although ^{31}P NMR data can be obtained more readily. Thus, $Hg(PPh_3)_2(ClO_4)_2$ has been examined by ^{31}P NMR methods but not by ^{199}Hg NMR.[6,7]

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(4) On leave from the Heyrovský Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.
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However, some data have been obtained for the more soluble perchlorate and tetrafluoroborate salts,[7,8] and results indicate a rich chemistry in terms of their interactions and coordination properties.[7]

In a recent communication from these laboratories[9] it was indicated that electrochemical data, which may be conveniently obtained at the 10^{-6} M concentration range with modern instrumental methods, may also be used to provide substantial information of the kind more traditionally obtained from NMR techniques.[10] Indeed when the two techniques may be applied to the same system, they provide complementary information, which may be included in the interpretation of data relevant to the other technique.

Electrochemical studies of mercury(II) complexes have produced a wide variety of mechanisms.[11] When mercury electrodes are used, the elemental mercury is usually involved in the electrode process. Many of the electrode processes are also very fast and involve unusual stoichiometry. Thus, for example, the reduction of HgX_2 (X = Cl, Br, I) in dimethylformamide occurs via a two-stage process[12]

$$3HgX_2 + 2e^- \rightleftharpoons 2HgX_3^- + Hg \qquad (7)$$

$$2HgX_3^- + 4e^- \rightleftharpoons 6X^- + 2Hg \qquad (8)$$

to give an overall process

$$HgX_2 + 2e^- \rightleftharpoons Hg + 2X^- \qquad (9)$$

while that for HgX_2P_2 (X = Cl, Br, I; P = phosphine) occurs in a one-step process[9]

$$HgX_2P_2 + 2e^- \rightleftharpoons Hg + 2X^- + 2P \qquad (10)$$

The electrochemistry of $[HgP_2]^{2+}$ in acetonitrile has been described briefly.[13] The overall electrode process is

$$[HgP_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P \qquad (11)$$

but mechanistic details are unknown.

In the present work, the detailed electrochemistries of the $[HgP_2]^{2+}$ complexes have been examined in dichloromethane. Examination of possible influences of ligand exchange and comparisons with reduction of HgX_2 and HgX_2P_2 are considered. Results are also compared with NMR data to further ascertain the usefulness of electrochemistry in detecting the presence of exchange reactions and in aiding the interpretation of NMR data and vice versa.

Experimental Section

$[HgP_2]^{2+}$ compounds were prepared as their perchlorate salts according to literature methods[6] while phosphine ligands were obtained from commercial sources and used without further purification. All other chemicals and solvents were of analytical grade purity.

Electrochemical data were obtained at 20 ± 1 °C in dichloromethane containing 0.1 M Bu_4NClO_4 as the supporting electrolyte. An EG & G PAR Model 174 polarographic analyzer was used to obtain polarograms. Controlled-potential electrolysis experiments were undertaken with a PAR Model 173 potentiostat/galvanostat. All electrochemical experiments were performed with a three-electrode system: working (mercury), auxiliary (platinum), and reference [Ag/AgCl (CH_2Cl_2–LiCl(satd))]. The particular electrode forms were appropriate to the form of the experiment, e.g., dropping-mercury electrode for polarography and mercury pool for controlled-potential electrolysis.

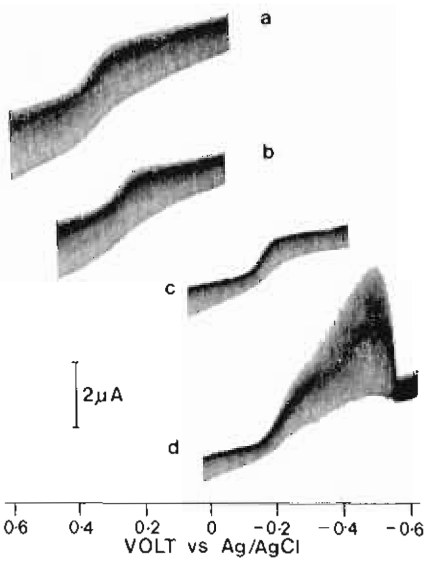

Figure 1. Dc polarograms for reduction of 2.5 × 10^{-5} M $[HgP_2]^{2+}$ compounds in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C: (a) $[Hg(P(C_6H_5)_3)_2]^{2+}$; (b) $[Hg(P(4\text{-}MeOC_6H_4)_3)_2]^{2+}$; (c) $[Hg(PBu_3)_2]^{2+}$; (d) $[Hg(P(C_6H_{11})_3)_2]^{2+}$. Drop time = 1 s.

Table I. Dc Polarographic Data for Reduction of 2.5 × 10^{-5} M $[HgP_2]^{2+}$ and Oxidation of P at the Dropping-Mercury Electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C (Drop Time 1.0 s)

	$[HgP_2]^{2+}$ data			$E_{1/2}$ for oxidn of P,[a] V vs. Ag/AgCl
ligand P	$E_{1/2}$, V vs. Ag/AgCl	$E_{1/4} - E_{3/4}$, mV	i_d, μA	
$P(2\text{-}MeC_6H_4)_3$	0.470	40	0.90	0.470
$P(4\text{-}FC_6H_4)_3$	0.360	45	0.94	0.360
$P(C_6H_5)_3$	0.350	49	1.00	0.350
$P(3\text{-}MeC_6H_4)_3$	0.300	45	0.93	*b*
$P(4\text{-}MeC_6H_4)_3$	0.280	49	0.91	0.280
$P(4\text{-}MeOC_6H_4)_3$	0.280	52	0.93	*b*
$P(4\text{-}ClC_6H_4)_3$	0.270	49	1.07	0.270
$P(2\text{-}MeOC_6H_4)_3$	0.040	52	0.83	0.040
PBu_3	−0.100	32	0.95	−0.100
$P(C_6H_{11})_3$	−0.190	53	0.91	−0.190[c]

[a] Concentration not accurately known because of decomposition. [b] Complicated by maxima, which introduce considerable uncertainty. [c] Very concentration dependent, but similar to $E_{1/2}$ for reduction of mercury complex at very dilute concentration.

NMR data were recorded on a JEOL FX 100 pulsed Fourier transform spectrometer with ^{31}P chemical shifts (ppm) being measured relative to external 85% H_3PO_4 while ^{199}Hg chemical shifts are reported relative to external 1 M phenylmercury acetate in dimethyl sulfoxide. High-frequency positive convention is used. Further details on the NMR instrumentation and measurement procedures are contained in ref 7 and 10.

Results and Discussion

Figure 1 shows dc polarograms for reduction of 2.5 × 10^{-5} M solutions of various $[HgP_2]^{2+}$ compounds, and Table I summarizes the data. This concentration is near the dc polarographic detection limit for reduction of the mercury compounds. Nevertheless, it was found that in these very dilute solutions the dc polarograms are very well-defined except for that of $[Hg((C_6H_{11})_3P)_2]^{2+}$ (Figure 1d), which has a pronounced maximum. At higher concentrations a range of complex behavior is observed; maxima and strong absorption over a wide potential range are indicated. An oxidation process is observed for all the ligands at potentials similar to those at

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(7) R. Colton and D. Dakternieks, *Aust. J. Chem.*, **34**, 323 (1981), and references cited therein.

(8) ^{199}Hg NMR data on the $[Hg(PMe_3)_2][BF_4]_2$ are presented in ref 5, p 268, as unpublished results by P. L Goggin, R. J. Goodfellow, and A. J. Griffiths.

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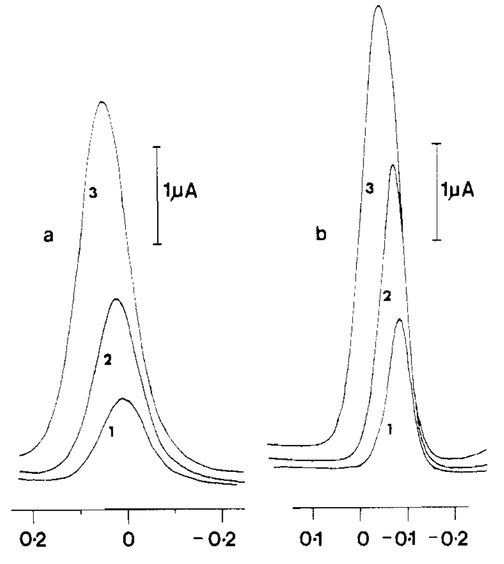

Figure 2. Differential-pulse polarograms for reduction of 2.5×10^{-5} M $[HgP_2]^{2+}$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C at amplitudes (1) −25 mV, (2) −50 mV, and (3) −100 mV: (a) $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$; (b) $[Hg(PBu_3)_2]^{2+}$. Drop time = 1 s.

which reduction of the corresponding $[HgP_2]^{2+}$ complex occurs. At even low concentrations in the 10^{-5} M concentration range distortions (maxima) are found for the ligand oxidations, and frequently more than one wave is observed at higher concentration. Many of the ligands are unstable in dichloromethane (dilute solution; oxygen sensitive to produce phosphine oxide). In contrast, the mercury complexes are far more stable, and the majority of quantitative studies were undertaken on the mercury complexes rather than on the ligands.

A large substituent effect particularly between alkyl- and arylphosphines is observed for reduction of $[HgP_2]^{2+}$ (large $E_{1/2}$ differences) (Figure 1), but for all the complexes the dc limiting current per unit concentration is essentially the same (see Table I). Furthermore, the dc limiting currents are diffusion controlled (diffusion current proportional to the square root of mercury column height), and the product of the reduction is P. Controlled-potential electrolysis experiments demonstrate that the overall process is a two-electron reduction and cyclic voltammetry is consistent with chemical reversibility. The overall electrode process for all complexes is therefore confirmed to occur as in eq 11.

Figure 2 contains two examples of differential-pulse polarograms for reduction of the mercury complexes at variable amplitude. Highly symmetric responses are observed, although the half-widths vary significantly with different compounds. In particular, the half-width of the $[Hg(PBu_3)_2]^{2+}$ complex is considerably narrower than for the reduction of the other complexes. If the electrode process were to occur directly via a two-electron step as in eq 11, theoretical work indicates considerable asymmetry would be expected.[11] For example, differential-pulse polarograms for reduction of HgX_2P_2 complexes[9,11] are very asymmetric under conditions of differential-pulse polarography where eq 10 has been suggested to be appropriate. The implication of this result is that the electrode process is first order with respect to charge transfer, unlike many other examples.[11]

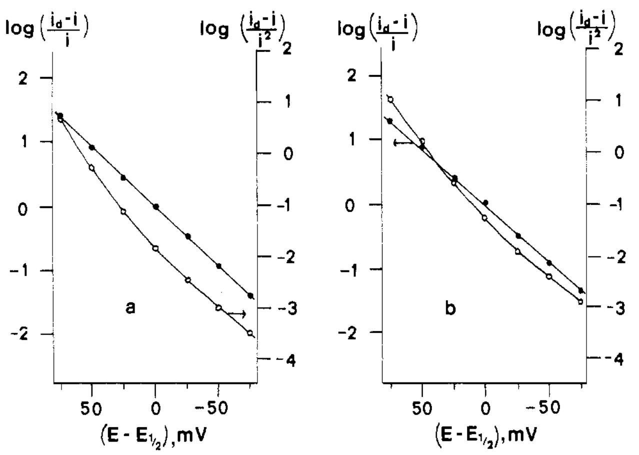

Figure 3. Plots of normalized potential vs. $\log[(i_d - i)/i]$ (●) and $\log[(i_d - i)/i^2]$ (○) for reduction of 1×10^{-4} M $[Hg(P(4\text{-}ClC_6H_4)_3)_2]^{2+}$ (a) and 5×10^{-5} M $[Hg(P(C_6H_{11})_3)_2]^{2+}$ (b) in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C. Drop time = 1 s.

Table II. Dependence of Differential-Pulse Peak Position, E_p, on Concentration for Reduction of $[Hg(P(2\text{-}MeC_6H_4)_3)_2]^{2+}$ in Dichloromethane at 20 °C (Drop Time 1.0 s)

	E_p, V vs. Ag/AgCl		
concn, M	−25 mV[b]	−50 mV[b]	−100 mV[b]
5×10^{-6}	0.472	0.487	0.512
1×10^{-5}	0.480	0.490	0.515
2×10^{-5}	0.482	0.493	0.520
4×10^{-5}	0.490	0.500	0.525
8×10^{-5}	0.487	0.499	0.522
1.6×10^{-4}	0.478	0.489	0.513
3.2×10^{-4} [a]	0.444	0.460	0.499

[a] Shoulder present. [b] Amplitude.

Figure 3 shows a plot from dc polarograms of E vs. $\log[(i_d - i)/i]$ (first order) and E vs. $\log[(i_d - i)/i^2]$ (second order) for some of the complexes (i_d = diffusion-controlled limiting current; i = direct current; E = dc potential). The linearity of the $\log[(i_d - i)/i]$ plot confirms the first-order nature of the process; if eq 11 had been appropriate, then the second-order plot would have been linear. The slope of the linear first-order plots shown in Figure 3a is 55 ± 2 mV for $[Hg(P(4\text{-}ClC_6H_4)_3)_2]^{2+}$, which is consistent with a one-electron charge-transfer step. Most of the other complexes give similar values, although they can be less as shown in Figure 3b, where the slope is only 46 ± 2 mV. Most other examples for reduction of mercury complexes at mercury involve a two-electron charge-transfer step, so this may be regarded as a surprising result. Table II provides some data for the dependence of differential-pulse peak position, E_p, on concentration. While E_p is not completely independent of concentration as theoretically predicted for a first-order reaction, the response is far removed from that theoretically predicted for second or higher order reactions.[11]

The presence of absorption would explain the small concentration dependence of E_p. Adsorption is readily revealed in the differential-pulse polarograms via other phenomena. For example, the response for the charging or background current without $[HgP_2]^{2+}$ is substantially modified by the presence of the compound. Tensammetric and related adsorption influences are well documented in the field of ac polarography[14,15] but are now becoming equally well recognized in the field of differential-pulse polarography.[16-18]

Figure 4 provides additional data obtained from differential-pulse polarography; the dependence of E_p vs. amplitude,

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Table III. Comparison of Phosphorus-31 and Mercury-199 NMR Data[a] for $[HgP_n]^{2+}$ in Dichloromethane

P	electrochem data, $E_{1/2}$, V vs. Ag/AgCl	n	NMR data				
			mercury complex			ligand	
			$\delta(^{199}Hg)^b$	$\delta(^{31}P)$	J(Hg,P)	$\delta(^{31}P)$	$\Delta\delta(^{31}P)$
$P(2\text{-}MeC_6H_4)_3$	0.470	2	230	39.7	4240	−29.9	69.6
$P(C_6H_5)_3$	0.350	2	*c*	47.2	5010	−5.3	52.5
		3	875	42.8	3120		48.1
		4	845	32.2	2090		37.5
$P(3\text{-}MeC_6H_4)_3$	0.300	2	285	46.1	5060	−5.2	51.3
		3	895	41.1	3090		46.3
		4	890	28.7	2070		33.9
$P(4\text{-}MeC_6H_4)_3$	0.280	2	200	47.2	4940	−8.0	55.2
		3	885	41.1	3080		49.1
		4	840	29.2	2090		37.2
$P(4\text{-}MeOC_6H_4)_3$	0.280	2	180	45.5	4800		
		3	880	41.1	3040		
		4	850	26.8	2070		
$P(4\text{-}ClC_6H_4)_3$	0.270	2	90	43.1	5340	−8.4	51.5
		3	770	40.3	3255		48.7
$P(2\text{-}MeOC_6H_4)_3$	0.040	2	190	3.3	4980	−38.5	41.8
PBu_3	−0.100	2	290	49.8	4280	−30.1	79.9
		3	1080	38.6	3050		68.7
		4	1130	4.8	1980		34.9
$P(C_6H_{11})_3$	−0.190	2	420	78.3	3730	10.8	67.7

[a] NMR data taken from ref 7. [b] $n = 2$, triplet; $n = 3$, quartet; $n = 4$, quintet. [c] Too insoluble for ^{199}Hg NMR.

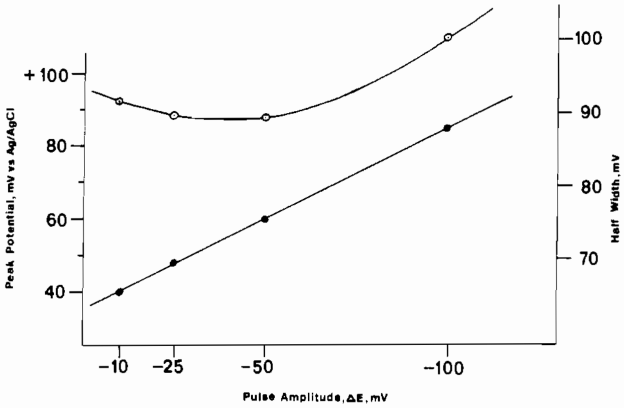

Figure 4. Plots of peak potential (●) and half-width (○) vs. pulse amplitude, ΔE, from differential-pulse polarograms for the reduction of 5×10^{-5} M $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C. Drop time = 1 s.

ΔE, is in excellent agreement with theory for a unity-order reaction. Furthermore, $E_{1/2} = E_p - \Delta E/2$ as required by theory. The half-width dependence on ΔE is not in exact agreement with theory and varies substantially from compound to compound. However, in combination with the dc results, all data are consistent with a one-electron charge-transfer step, with coupled chemical reactions occurring at the electrode surface (reactant and product adsorption). The observation that the dc polarograms and differential-pulse polarograms have slopes of log $[(i_d - i)/i]$ and half-width, respectively, less than Nernstian is consistent with adsorption phenomena.[19]

The above data can be accommodated by the reaction scheme shown in (12)–(14), which requires that all equilibria

$$[HgP_2]^{2+} + Hg \rightleftharpoons 2[HgP]^+ \tag{12}$$

$$2[HgP]^+ + 2e^- \rightleftharpoons 2Hg + 2P \tag{13}$$

$$[HgP_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P \tag{14}$$

are established rapidly and is closely related to that proposed for oxidation of the potentially bidentate dithiocarbamate ligand at mercury electrodes.[20] However, it needs to be noted how different the reaction scheme is compared with the reduction of HgX_2P_2[9] or $[Hg(CN)_n]^{(n-2)+}$ (n = 2–4).[21] The existence of a monomeric mercury(I) intermediate may offer an explanation for the different behavior since mercury(I) halides and pseudohalides tend to exist as dimeric species.

Several aspects of the proposed reaction scheme can be tested by a combination of electrochemical and NMR measurements. Some experiments may be more informative than usual because of the unusual nature of the electrochemical reduction scheme.

Mixing mercury(I) perchlorate and phosphine ligands in dichloromethane produces elemental mercury (visual identification) and $[HgP_2]^{2+}$ (electrochemical identification), which is consistent with the postulate that the disproportionation step represented by eq 12 lies substantially to the left.

Solutions containing 1:1 stoichiometries of mercury(II) perchlorate and phosphine produce electrochemical data consistent with formation of $[HgP_2]^{2+}$ and unreacted mercury(II) perchlorate. Further addition of phosphine produces a negative current component to the dc polarograms. That is, the polarographic response is consistent with the reduction of $[HgP_2]^{2+}$ producing positive dc current and added to this is the negative current for oxidation of phosphine in the presence of mercury or current arising from the reverse of the reaction scheme presented in eq 12–14. Some of the surface properties are however modified at higher concentrations, particularly maxima and related phenomena. NMR data[7] confirm the electrochemistry with respect to the addition of 1 mol of phosphine to mercury(II) perchlorate. However, if further phosphine is added to $[HgP_2]^{2+}$, with some phosphines, it is clear from the NMR data that $[HgP_3]^{2+}$ and $[HgP_4]^{2+}$ can be formed. Some of the NMR data from the literature are given in Table III. NMR data reveal that mercury–phosphorus coupling can be seen for some complexes at 30 °C, whereas for others lower temperatures are required.[7] The implication from the NMR data is that $[HgP_2]^{2+}$ alone is not formed at room temperature and that rapid exchange (on the NMR time scale) occurs between the various $[HgP_n]^{2+}$ species (n = 2–4).

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Electrochemical data do not show separate polarographic reduction waves that can be associated with the existence of $[HgP_3]^{2+}$ or $[HgP_4]^{2+}$ as noted with HgX_3^-,[12] and any indication of their existence from an electrochemical point of view is masked by the unity order of the charge-transfer process. This result further confirms the postulated reaction mechanism because, irrespective of the coordination number, the lability of the complexes enables eq 13 to control the charge transfer. The contrast with reduction of $[Hg(CN)_n]^{(n-2)+}$ ($n = 2–4$) or oxidation of mercury in the presence of CN^- is quite surprising since similar mercury(II) species appear to be present.[21] In the case of the cyanides the order of the electrode process changes with concentration even though separate reduction waves are not observed and $E_{1/2}$ is dependent on cyanide concentration as expected for a non-unity-order charge-transfer process.

Data in Table III show that electrochemical data do not correlate in a linear fashion with any of the NMR parameters. Since steric effects appear to be important in determining the chemical shifts of ^{31}P and ^{199}Hg and other NMR parameters, this lack of a linear free energy relationship is predicted.[22] $E_{1/2}$ directly reflects the change in base strength or relative stability constant, K, associated with reaction 15. That is, $E_{1/2}$ is

$$Hg^{2+} + 2P \overset{K}{\rightleftharpoons} [HgP_2]^{2+} \qquad (15)$$

expected to be closely allied with electronic effects. The large difference in $E_{1/2}$ between the 2-Me and 2-MeO derivatives is probably the only surprising result in this context. However, the influence of steric effects with the two techniques would not appear to be parallel. The lack of a linear correlation between $\delta(^{199}Hg)$ and $\delta(^{31}P)$ confirms that additivity of substituent effects does not occur in the NMR data.

The nature of the large $E_{1/2}$ variation with ligand implies that, while it is not possible to detect exchange between $[HgP_2]^{2+}$ and P (same P) electrochemically, it may be possible to detect exchange between $[HgP_2]^{2+}$ and $[HgP'_2]^{2+}$ ($P \neq P'$) or upon addition of $[HgP_2]^{2+}$ to P′. Indeed some most interesting consequences could arise from thermodynamic considerations.

Consider two redox couples with standard redox potentials $E_1°$ and $E_2°$ (the mercury(I) intermediate deduced from polarography is now omitted from the discussion for simplicity):

$$[HgP_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P \quad (E_1°) \qquad (16)$$

$$[HgP'_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P' \quad (E_2°) \qquad (17)$$

Assuming that $E_2°$ is more negative than $E_1°$ implies that, if both $[HgP_2]^{2+}$ and P′ are present, reactions will occur in the following manner:

$$[HgP_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P \qquad (18a)$$

$$Hg + 2P' \rightleftharpoons [HgP'_2]^{2+} + 2e^- \qquad (18b)$$

that is

$$[HgP_2]^{2+} + 2P' \rightleftharpoons [HgP'_2]^{2+} + 2P \qquad (19)$$

with the equilibrium position in eq 19 lying to the right. The equilibrium constant K for eq 19 can be calculated from the value ($E_2° - E_1°$). Clearly, the presence of mercury can catalyze exchange reactions at the electrode surface. The presence of mercury(I) could also catalyze the exchange reactions. Note that, while elementary mercury appears in both eq 18a and 18b, it is absent from eq 19 and that the equilibrium constant K does not contain a term involving mercury(I) or mercury(0).

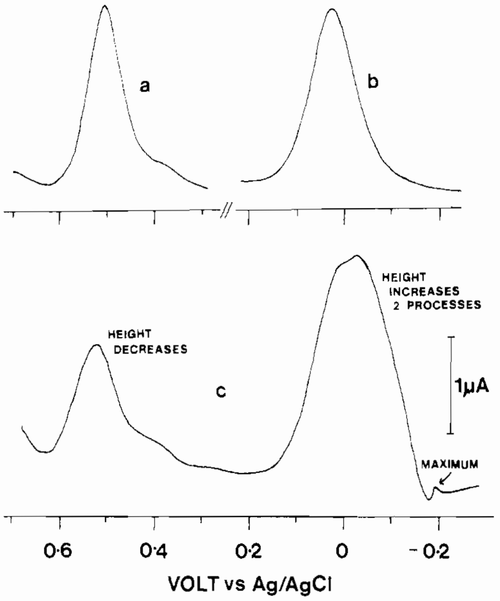

Figure 5. Differential-pulse polarograms in dichloromethane (0.1 M Bu_4NClO_4) for reduction of individual solutions of 5×10^{-5} M $[Hg(P(2\text{-}MeC_6H_4)_3)_2]^{2+}$ (a) and 5×10^{-5} M $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$ (b) compared with polarograms of a solution containing 5×10^{-5} M of both compounds (c). Temperature = 20 °C, drop time = 1 s, and amplitude = −100 mV.

Consider also the situation if the reaction

$$[HgP_2]^{2+} + [HgP'_2]^{2+} \rightleftharpoons 2[HgPP']^{2+} \qquad (20)$$

occurs in the bulk solution. It may be supposed that the hypothetical reaction

$$[HgPP']^{2+} + 2e^- \rightleftharpoons Hg + P + P' \qquad (21)$$

would have an $E_3°$ value of approximately $(E_1° + E_2°)/2$ V. However, if reduction of $[HgPP']^{2+}$ were to occur at a mercury electrode, the potential at which one of the products, P, was generated would be at a value where oxidation to produce $[HgP_2]^{2+}$ occurs. That is, the reverse of reaction 20 may occur at an electrode surface whereas in the bulk solution exactly the opposite occurs. The polarography of mixtures of $[HgP_2]^{2+}$ and P′ or $[HgP_2]^{2+}$ and $[HgP'_2]^{2+}$ could therefore have unusual properties compared with those of individual solutions. Thus, the reduction current from $[HgP_2]^{2+}$ would be nulled by the oxidation of P′ in the presence of mercury, unless an exchange reaction occurred at the electrode surface as in eq 22. With

$$[HgP_2]^{2+} + 2P' \rightleftharpoons [HgP'_2]^{2+} + 2P \qquad (22)$$

this rearrangement, oxidation of P and reduction of $[HgP'_2]^{2+}$ would appear to occur even though in bulk solution neither of these species is present.

Figure 5 shows a comparison of differential-pulse polarograms of $[Hg(P(2\text{-}MeC_6H_4)_3)_2]^{2+}$ and $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$ in individual solutions and in a mixture. This combination was chosen because no higher complexes are formed (see Table III; NMR data) and also because their $E_{1/2}$ values are well separated. The $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$ complex ($[HgP'_2]^{2+}$) is reduced at more negative potential than the $[Hg(P(2\text{-}MeC_6H_4)_3)_2]^{2+}$ complex ($[HgP_2]^{2+}$). On addition of $[HgP'_2]^{2+}$ to $[HgP_2]^{2+}$ the differential-pulse peak height of $[HgP_2]^{2+}$ decreases. Conversely, the $[HgP'_2]^{2+}$ response increases in height and broadens because of the presence of an extra process. Furthermore, a maximum occurs at negative potentials, which is not evident in the individual polarograms. The maximum appears as a negative current in the differen-

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[22] A. M. Bond, S. W. Carr, R. Colton, and D. P. Kelly, *Inorg. Chem.*, in press.

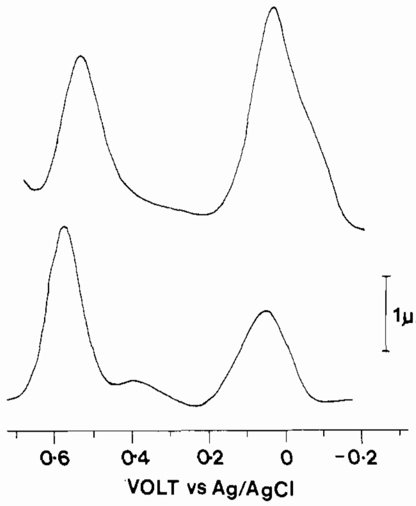

Figure 6. Drop time and temperature dependence of the mixture of compounds shown in Figure 5c. In the upper curve the drop time has been changed to 0.5 s, and in the lower curve the temperature has been lowered to −35 °C.

tial-pulse polarogram shown in Figure 5. Clearly, these phenomena are qualitatively explicable in terms of reactions at the electrode surface (eq 23–29). These equations are

$$[HgP_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P \qquad (23)$$

$$P + [HgP'_2]^{2+} \rightleftharpoons [HgPP']^{2+} + P' \qquad (24)$$

$$2[HgPP']^{2+} \rightleftharpoons [HgP_2]^{2+} + [HgP'_2]^{2+} \qquad (25)$$

$$P + [HgPP']^{2+} \rightleftharpoons [HgP_2]^{2+} + P' \qquad (26)$$

$$[HgP_2]^{2+} + 2P' \rightleftharpoons [HgP'_2]^{2+} + 2P \qquad (27)$$

$$[HgPP']^{2+} + 2e^- \rightleftharpoons Hg + P + P' \qquad (28)$$

$$[HgP'_2]^{2+} + 2e^- \rightleftharpoons Hg + 2P' \qquad (29)$$

written in their simplified form, without employing mercury(I) intermediates. The observed curves are extremely time and temperature dependent as shown in Figure 6 and also concentration dependent (not shown). The presence of second or higher order chemical reactions is evident.

When P′ was added to $[HgP_2]^{2+}$ at −35 °C in the presence of elemental mercury, time-dependent reactions were observed in the bulk of the solution as ascertained by electrochemical monitoring but the end result approached that for a mixture of $[HgP_2]^{2+}$ plus $[HgP'_2]^{2+}$. Clearly, in the presence of mercury, the system can adjust to the thermodynamically expected result, but not all the reactions are extremely rapid. Furthermore, the possibility of other mercury complexes such as HgP_2P' or $HgP_2P'_2$ being formed at the electrode surface cannot be discounted.

With the present knowledge of the chemistry of these mercury complexes and electrochemical theory, no quantitative understanding of the reactions is possible. However, theoretical studies on far simpler situations are available[23-27] and demonstrate that the observations are intuitively consistent with the above reaction schemes.

Mixtures containing equimolar quantities of $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$ and $[Hg(P(2\text{-}MeC_6H_4)_3)_2]^{2+}$ were too insoluble in dichloromethane for NMR studies. The nature of the precipitate is unknown, but obviously a reaction does occur when the two compounds are mixed.

Dichloromethane solutions of $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$ containing an excess of $P(2\text{-}MeC_6H_4)_3$ resulted in the formation of some elemental mercury and other materials, but at 30 °C both ^{31}P and ^{199}Hg NMR data show only the presence of $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$ and free $P(2\text{-}MeOC_6H_4)_3$ as soluble species. Cooling these solutions caused further precipitation, thus preventing further NMR studies at lower temperatures. The presence of elemental mercury and precipitation of compounds confirm that complex reactions do occur and indicate the limitations and difficulties in interpreting the NMR data.

Experiments with mixtures including $[Hg(PBu_3)_2]^{2+}$, where higher coordination is possible (n = 2–4; as shown in Table III), produced even more complex polarograms than with mixtures of $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{+}$ and $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$. Electrochemical data indicate that exchange reactions are probably redox modified by the presence of different forms of mercury. There was no evidence from NMR measurements of the formation of soluble mixed species $[HgPP']^{2+}$ for any Hg:P:P′ stoichiometry of the phosphines studied. The only soluble mercury species containing different phosphine groups were of the stoichiometry $[HgP_2P']^{2+}$ and were identified by the presence of AB_2X-type NMR spectra. Nevertheless, the NMR data reveal that mixed-ligand complexes can be formed.

The unusual features of the electrochemical exchange reactions observed in this work are governed by the fact that $E_{1/2}$ values for reduction of the complex and oxidation of the free ligand are identical at mercury electrodes. By contrast, HgX_2P_2[9] is reduced at potentials more negative than those of oxidation of either X^- or P at mercury electrodes. The unity order of the electron transfer may be associated with the unusual stability of say $[HgP]^+$. With halides, mercury(I) species are usually dimeric (sometimes insoluble).

In summary, the area of mercury phosphine electrochemistry has many complex and unusual features, which are as yet not always well understood. Electrochemical and NMR experiments are being continued in these laboratories in an endeavor to further understand the chemical principles associated with mercury chemistry.

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Registry No. $[Hg(P(2\text{-}MeC_6H_4)_3)_2]^{2+}$, 71087-41-7; $[Hg(P(4\text{-}FC_6H_4)_3)_2]^{2+}$, 71087-37-1; $[Hg(P(C_6H_5)_3)_2]^{2+}$, 47807-66-9; $[Hg(P(3\text{-}MeC_6H_4)_3)_2]^{2+}$, 77630-93-4; $[Hg(P(4\text{-}MeC_6H_4)_3)_2]^{2+}$, 47856-90-6; $[Hg(P(4\text{-}MeOC_6H_4)_3)_2]^{2+}$, 47879-91-4; $[Hg(P(4\text{-}ClC_6H_4)_3)_2]^{2+}$, 71087-35-9; $[Hg(P(2\text{-}MeOC_6H_4)_3)_2]^{2+}$, 77452-08-5; $[Hg(PBu_3)_2]^{2+}$, 77135-70-7; $[Hg(P(C_6H_{11})_3)_2]^{2+}$, 66119-62-8; $P(2\text{-}MeC_6H_4)_3$, 6163-58-2; $P(4\text{-}FC_6H_4)_3$, 18437-78-0; $P(C_6H_5)_3$, 603-35-0; $P(4\text{-}MeC_6H_4)_3$, 1038-95-5; $P(4\text{-}ClC_6H_4)_3$, 1159-54-2; $P(2\text{-}MeOC_6H_4)_3$, 4731-65-1; PBu_3, 998-40-3; $P(C_6H_{11})_3$, 2622-14-2.

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