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Comparison of Electrochemical Data for Reduction of Mercury(II) Dihalide Diphosphine Complexes in Dichloromethane and ^{199}Hg and ^{31}P NMR Data

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Detailed electrochemical studies have been carried out on the reduction of a series of HgX_2P_2 complexes ($X = Cl^-, Br^-, I^-$; P = tertiary phosphine) in CH_2Cl_2 solution. At a Hg electrode, the complexes exhibit reversible two-electron reductions of unusual stoichiometry: $HgX_2P_2 + 2e^- \rightleftharpoons Hg + 2X^- + 2P$. The reduction potentials correlate well with $\delta(^{31}P)$, $\delta(^{199}Hg)$, and $J_{P,Hg}$ NMR data. Electrochemical characterization of the halide-exchange reactions $HgX_2P_2 + HgX_2P_2 \rightleftharpoons 2HgXX'P_2$ is in excellent agreement with NMR observations. However, electrochemical data reveal that phosphine-exchange reactions are substantially different in nature from the halide-exchange reactions. The combined use of electrochemical and NMR measurements readily enables several features of the different halide- and phosphine-exchange reactions to be unraveled.

Introduction

Nuclear magnetic resonance spectroscopy (NMR) has become one of the major techniques for structural determination of compounds in solution. Kinetic and thermodynamic information on interactions between solute and solvent, exchange reactions, the rigidity of molecules, and other areas of wide interest have been greatly aided by the use of proton NMR.[4,5] The relatively recent advent of commercially available pulsed-Fourier-transform NMR spectrometers has made it possible for many workers to measure the NMR spectra of a wide range of nuclei. Access to information on the NMR response of nuclei of many elements should prove as advantageous to inorganic and organometallic chemists as has ^{13}C and ^{1}H spectra to the organic chemist, and the importance of the new advances is therefore readily appreciated.

There are still many limitations on the use of NMR in inorganic chemistry. Many elements and inorganic compounds cannot be examined by this spectroscopic technique, and frequently very high concentrations of compound are required to achieve adequate sensitivity. Furthermore, the technique is most favorably used for studies on solution chemistry only when diamagnetic compounds are involved, leaving a large range of paramagnetic compounds unavailable for examination, except in specialized areas of application. Electrochemical techniques are also widely used in solution studies of inorganic compounds, and on some occasions correlations between the two techniques have proved useful. For example, Gutmann et al.[6] in a study of the outer-sphere effects of different solvents on $[Co(en)_3]^{3+}$ (en = ethylenediamine) used the correlation between the polarographic half-wave potentials for the $[Co(en)_3]^{3+}/[Co(en)_3]^{2+}$ couple and the ^{59}Co NMR chemical shift of $Co(en)_3(ClO_4)_3$ to prove that the outer-sphere solvation of $[Co(en)_3]^{3+}$ is accompanied by an increase in electron density at the Co atoms with increasing donor numbers of the solvent. In an entirely different area of application, ^{13}C NMR spectra chemical shifts and $J(^{13}C-^{199}Hg)$ coupling constants have also been correlated with polarographic and other data in a study of the σ,π conjugation in some organomercurial systems.[7]

Careful consideration of the principles and processes associated with electrochemical reduction and oxidation combined with several specific examples available in the literature led us to believe that, in general terms, much of the information frequently extracted from NMR data should also be inherently present in the electrochemical experiment. On the other hand, in several important areas the two techniques are complementary. The combined use of these two techniques should therefore prove to provide a powerful approach to understanding the nature of electrode processes and solution chemistry in the organometallic field.

The present study examines the reduction at a mercury electrode of a series of HgX_2P_2 complexes [X = Cl, Br, I; P = tri-*n*-butylphosphine (PBu_3), triphenylphosphine (PPh_3), tris(4-methoxyphenyl)phosphine (pmp)] in dichloromethane. These compounds were chosen for several reasons. First, the compounds are simple tetrahedral molecules[8] where products after complete electrochemical reduction are likely to be elemental mercury, free halide, and free phosphine. Thus, unlike the majority of redox processes where both halves of the redox process consist of compounds whose characteristics all need to be well-known, the redox system chosen has some simplifying features with respect to the nature of the products. Second, the compounds are soluble in the noncoordinating solvent, dichloromethane, which is a suitable medium for both electrochemical and NMR studies without problems arising from competitive reactions from the solvent. Third, ^{31}P and ^{199}Hg NMR studies are among the most suitable available, with a nuclear spin I of $^1/_2$ and adequate sensitivity. ^{31}P and ^{199}Hg NMR spectra of mercury(II) halide phosphine complexes have been reported previously.[9-17] Finally, exchange reactions are known to occur so that detailed comparisons with electrochemical data can be made in a range of areas of general interest.

Experimental Section

The mercury(II) dihalide diphosphine complexes were prepared as described previously.[10,18] Electrochemical experiments were carried

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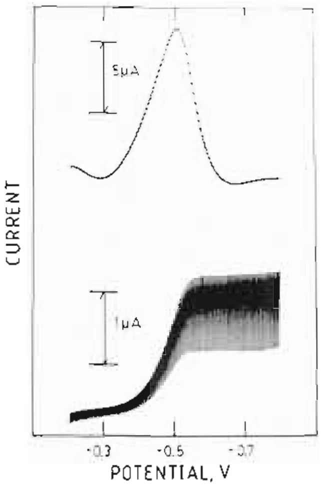

Figure 1. Polarographic reduction of 5.34×10^{-4} M $HgBr_2(PBu_3)_2$ in dichloromethane (0.1 M Bu_4NClO_4). Upper curve is a differential pulse polarogram using a −50-mV pulse amplitude; lower curve is a dc polarogram. Drop time was 1.0 s, and temperature was 20 °C.

out at 20 ± 1 °C in analytical reagent grade CH_2Cl_2 (BDH Chemicals) containing 0.1 M tetrabutylammonium perchlorate (Eastman Kodak) as supporting electrolyte. Concentration-dependent polarographic maxima were observed for all complexes Electrochemical measurements were performed only on solutions sufficiently dilute that maxima were not observed.

A PAR Model 174 polarographic analyzer equipped with a PAR Model 172 drop timer was employed to obtain dc and differential-pulse polarograms. Solutions were degassed with nitrogen and maintained under nitrogen during each experiment. The reference electrode was a Ag/AgCl element immersed in CH_2Cl_2 saturated with LiCl and isolated from the test solution by a medium porosity glass frit.

Half-wave potentials were determined from dc polarograms by analyzing the experimental polarograms mathematically according to eq 2 and 3 with utilization of linear regression analysis to establish the best fit to the data. The relationship between the peak potential of differential-pulse polarograms and the polarographic half-wave potential depends on both the stoichiometry of the electrode process and the modulation amplitude employed.[19,20] Account was also taken of the instrumental distortion inherent in the PAR 174 instrument.[21] Half-wave potentials for the mixed complexes and for solutions below 10^{-4} M were computed from observed differential-pulse peak potentials.

The ^{31}P and ^{199}Hg NMR data quoted were either taken from the literature[11,16,17] or measured with use of the instrumentation described in ref 16 and 17. The ^{31}P chemical shifts are referenced against 85% phosphoric acid; the ^{199}Hg chemical shifts are referenced against 1 M phenylmercury acetate in dimethyl sulfoxide.

Oxidation waves associated with HgX_2P_2 complexes were observed but are not discussed in this report which solely concerns the well-defined reduction steps.

Results and Discussion

(a) Reduction of HgX_2P_2 Complexes. Figure 1 shows a dc polarogram for reduction of $HgBr_2(PBu_3)_2$ in dichloromethane and the differential-pulse polarogram for the same solution. The polarographic reduction wave for all compounds was observed to be well-defined in dichloromethane at concentrations below 5×10^{-4} M. However, pronounced maxima were observed at higher concentrations for some of the compounds. All data tabulated were obtained under conditions where maxima are absent.

Equimolar solutions of PPh_3 and halide ion produced a dc polarographic oxidation wave with the same half-wave potential as that for reduction of a solution of the appropriate mercury(II) dihalide diphosphine complex. Cyclic voltammetry at a slowly growing dropping mercury electrode showed well-defined peaks in both the negative (reduction) and positive (oxidation) scan directions. Both these results provide convincing evidence that the electrode process is reversible.

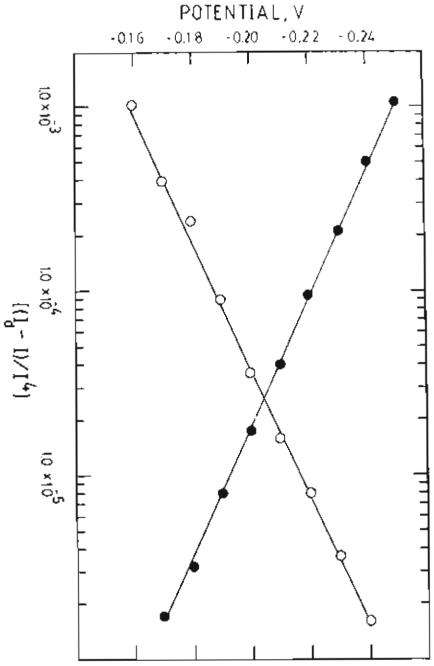

Figure 2. Logarithmetic analysis of dc polarograms in dichloromethane (0.1 M bu_4NClO_4): (○) reduction of 6.81×10^{-4} M $HgBr_2(PPh_3)_2$ with slope = 28.3 ± 1 mV and $E_{1/2} = -206.4$ mV; (●) oxidation of 6.90×10^{-4} M Bu_4NBr + 6.95×10^{-4} M PPh_3 with slope = 26.3 ± 1 mV and $E_{1/2} = -213.3$ mV. Drop time is 1.0 s, and temperature is 20 °C.

The simplest reversible electrode process for reduction of HgX_2P_2 complex is as in eq 1. While it may be unusual to

$$HgX_2P_2 + 2e^- \rightleftharpoons Hg + 2X^- + 2P \qquad (1)$$

postulate electrochemical reactions with this relatively complex and unusual stoichiometry as reversible under polarographic conditions, the above evidence indicates that this possibility must be explored.

The shape of the dc polarogram expected from the electrode process given in eq 1 is easily derived by application of the Nernst and Ilkovic equation:[22]

$$E = E_{1/2} + \frac{3RT}{2F} \ln (i_d/2) + \frac{RT}{2F} \ln [(i_d - i)/i^4] \qquad (2)$$

where

$$E_{1/2} = E^\circ + \frac{2RT}{F} \ln \left[\frac{D_P^{1/4} D_X^{1/4}}{4D_{HgX_2P_2}^{1/2}} \right] - \frac{3RT}{2F} \ln \left[\frac{C_{HgX_2P_2}}{2} \right] \qquad (3)$$

D_P, D_X, $D_{HgX_2P_2}$ are diffusion coefficients, and $C_{HgX_2P_2}$ is the bulk concentration of HgX_2P_2; the remaining symbols have their usual electrochemical significance.[22]

These equations predict the following. (1) A plot of E vs. log $[(i_d - i)/i^4]$ should be linear with a slope of $2.303RT/2F$ (29.1 mV at 20 °C). (2) A plot of $E_{1/2}$ vs. log $(C_{HgX_2P_2}/2)$ should be linear with a slope of $-3(2.303RT)/2F$ (−87.2 mV at 20 °C)

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Table I. Half-Wave Potentials of Individual Complexes

compd	$E_{1/2}$,[a] V	slope,[b] V
$HgCl_2(PBu_3)_2$	−0.456	0.029
$HgBr_2(PBu_3)_2$	−0.484	0.029
$HgI_2(PBu_3)_2$	−0.555	0.031
$HgCl_2(PPh_3)_2$	−0.210	0.035
$HgBr_2(PPh_3)_2$	−0.234	0.028
$HgI_2(PPh_3)_2$	−0.313	*c*
$HgCl_2$(pmp)$_2$	−0.291	0.041
$HgBr_2$(pmp)$_2$	−0.313	0.033
HgI_2(pmp)$_2$	−0.336	0.034
$(C_2H_5)_4NCl$	−0.126	
$(C_4H_9)_4NBr$	−0.191	
$(C_4H_9)_4NI$	−0.309	

[a] Evaluated at 0.001 M. [b] Plot of E vs. log $[(i_d - i)/i^4]$. [c] Determined by differential-pulse polarography.

Table II. Effect of Free Halide and Phosphine on $E_{1/2}$

$10^4 \times [Br^-]$,[a] M	$E_{1/2}$, mV	$10^4 \times [PPh_3]$,[a] M	$E_{1/2}$, mV	$10^4 \times [Br^-]$,[b] M	$E_{1/2}$, mV
0	−215	0	−215	0	−467
0.691	−220	0.693	−215	2.34	−470
1.73	−232	1.73	−215	5.85	−487
3.45	−245	3.47	−217	11.70	−495
6.91	−263	6.93	−217		

[a] 3.39×10^{-4} M $HgBr_2(PPh_3)_2$. [b] 5.34×10^{-4} M $HgBr_2(PBu_3)_2$.

Figure 2 shows the E vs. log $[(i_d - i)/i^4]$ plot for reduction of $HgBr_2(PPh_3)_2$ and oxidation of approximately equimolar concentrations of tetrabutylammonium bromide and triphenylphosphine; slopes (apart from sign) and intercepts to give $E_{1/2}$ are close to values predicted theoretically. Results for all compounds are presented in Table I. The HgX_2P_2 series conform very closely to the theoretical predictions for all compounds when P = PBu_3, but when P = PPh_3 or pmp, agreement between theory and experiment is not always as exact. Reasons for the partial nonideal behavior of the latter two series of complexes will be discussed at a later point in the text.

The $E_{1/2}$ dependence on concentration was examined experimentally and found to be in close agreement with the theoretically predicted result. Thus, at 20 °C and over the concentration range of 1.53×10^{-3}–4.9×10^{-5} M, a plot of $E_{1/2}$ vs. log $[HgCl_2(PBu_3)_2]$ was linear with a slope of −88.7 ± 0.7 mV. The theoretically predicted slope is −87.2 mV at 20 °C, and agreement with experiment is excellent.

Polarograms of solutions containing both $HgBr_2(PBu_3)_2$ and Bu_4NBr were found to have both a wave due to the reduction of the complex and a well-separated wave due to the oxidation of mercury in the presence of bromide.[23] Addition of bromide to the $HgBr_2(PPh_3)_2$ complex leads to the observation of a composite oxidation/reduction wave rather than individual waves because of similar half-wave potentials. The differential-pulse peak current and polarographic limiting current for the complex were unchanged by the addition of bromide to either complex; however, $E_{1/2}$ was observed to shift in a negative direction with increasing bromide concentration (Table II).

The theory for the electrode process in the presence of excess halide would predict that a wave shape change would accompany the shift in potential. In the limiting case where a very large excess of halide is present, it would be expected that the $E_{1/2}$ value would depend on ln $[(i_d - i)/i^2]$. Such theoretical expectations are not exactly realized, although behavior approximates the theory with respect to direction of $E_{1/2}$ shift and direction of wave shape change. ^{199}Hg and ^{31}P NMR spectra and $J_{Hg,P}$ coupling constants for $HgBr_2(PBu_3)_2$ were unaltered on addition of Bu_4NBr. One molar solutions of $HgBr_2(PBu_3)_2$ were used in the experiments to obtain adequate ^{199}Hg NMR sensitivity (in contrast to 10^{-3} M solutions or less in the electrochemical work), and bromide concentrations were examined over the concentration range 0.5–4.0 M. The NMR data demonstrate that halide does not displace phosphine nor does it provide any evidence for additional halide coordination. Any departures from theory are therefore not accounted for by reaction in the bulk solution. In solutions containing free halide, mercury is readily and reversibly oxidized. Because of the proximity of the $E_{1/2}$ for mercury oxidation and the $E_{1/2}$ for the reduction of HgX_2P_2 (Table I), the solution near the electrode will contain a small quantity of HgX_2 even at potentials where HgX_2P_2 is reduced. A reaction within the diffusion layer between HgX_2 and HgX_2P_2 will produce one or more of the halide-rich oligomers $Hg_2X_4P_2$, $Hg_3X_6P_2$, $Hg_4X_8P_2$, etc., whose chemistry is well-known.[8,16–18] In the simplest case

$$HgX_2 + HgX_2P_2 \rightleftharpoons Hg_2X_4P_2 \tag{4}$$

Cross redox reactions of this sort are well-known in electrochemistry.[22] The reactions must be rapid to account for the dependence of $E_{1/2}$ on bromide concentration and occur only within the diffusion layer, hence eq 1 still accurately describes the electrode process in the absence of free halide. Quantitative treatment of this aspect of the electrochemistry was not attempted because the appropriate equilibrium constants were unavailable; furthermore the appropriate diffusion/kinetic equations have not been solved for any electrode mechanism with the stoichiometry of eq 1.

It was noted earlier that the experiment vs. theory correlations were excellent for the $HgX_2(PBu_3)_2$ series. With the $HgX_2(PPh_3)_2$ and HgX (pmp)$_2$ series, the electrode processes due to reduction of HgX_2P_2 and oxidation of mercury in the presence of X^- occur at very similar potentials. Diffusion layer reactions between HgX_2 and HgX_2P_2 are most likely the cause of the poor agreement with eq 2 observed for some of the PPh_3 and pmp complexes (Table I). Reduction of $HgX_2(PBu_3)_2$ occurs at considerably more negative potentials than oxidation of mercury in the presence of X^-; hence the complications associated with the other phosphine complexes would not occur. Two partially resolved waves were observed in polarograms of $HgI_2(PPh_3)_2$ whose $E_{1/2}$ is nearly identical with that for the oxidation of mercury in the presence of I^-. The $E_{1/2}$ given in Table I was obtained from the larger of the two unresolved differential-pulse peaks.

Addition of free PPh_3 to solutions of $HgBr_2(PPh_3)_2$ results in an increase in the wave corresponding to oxidation of mercury in the presence of triphenylphosphine[24] but leaves the differential pulse peak potential (or $E_{1/2}$) and differential-pulse peak current (or i_d) unaltered for the reduction wave of the mercury complex (Table II).

The electrochemical data implies that a change in mechanism of the electrode process occurs on addition of phosphine as a dependence of $E_{1/2}$ on phosphine concentration would be expected if behavior analogous to bromide addition experiments had occurred. Addition of PBu_3 to solutions of $HgX_2(PBu_3)_2$ and measurements of ^{199}Hg and ^{31}P NMR

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(23) Oxidation of mercury in the presence of halide in dichloromethane can be represented by equations of the type $nX^- + Hg \rightleftharpoons HgX_n + 2e^-$. The value of n in dichloromethane is unknown but from studies in other solvents, e.g., Y. Matsui, et al., *Bull. Chem. Soc. Jpn.*, **41**, 2914 (1968); **43**, 1707, 2046, (1970); **43**, 2052 (1970), the processes involved can be complex and involve interactions of mercury halides of different stoichiometries.

(24) L. Horner and J. Haufe, *Chem. Ber.*, **101**, 2921 (1968) have reported an overall process $2PPh_3 + Hg \rightleftharpoons Hg(PPh_3)_2^{2+} + 2e^-$ in certain solvents, but the equation describing the electrode process in dichloromethane is unknown.

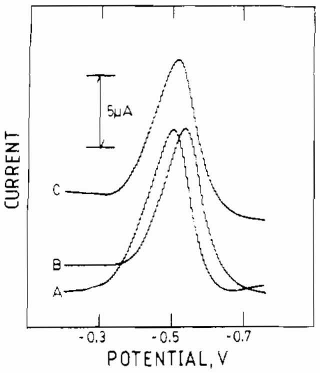

Figure 3. Differential-pulse polarographic reduction of $HgCl_2(PBu_3)_2$ + $HgI_2(PBu_3)_2$ in dichloromethane (0.1 M Bu_4NClO_4): A, 4.50 × 10^{-4} M $HgCl_2(PBu_3)_2$; B, 4.41 × 10^{-4} M $HgI_2(PBu_3)_2$; C, 2.25 × 10^{-4} M $HgCl_2(PBu_3)_2$ + 2.20 × 10^{-4} M $HgI_2(PBu_3)_2$. Pulse amplitude is −50 mV, drop time is 1.0 s, and temperature is 20 °C.

spectra reveal that distinct differences are also associated with the NMR data. On addition of bromide, no change in NMR data was observed. By contrast, rapid phosphine exchange is observed on the NMR time scale in the presence of PBu_3 at 30 °C. At lower temperatures, the exchange reactions can be slowed and an NMR spectrum attributable to $HgX_2(PBu_3)_3$ is observed. Electrochemical data demonstrate that no halide is released by addition of phosphine. Further addition of PBu_3 leads to the observation of the NMR spectrum of a $HgX_2(PBu_3)_3$ and free phosphine. Clearly reaction 5 can be important in phosphine addition experiments. The presence of

$$HgX_2P_2 + P \rightleftharpoons HgX_2P_3 \qquad (5)$$

this equilibrium reaction is consistent with the electrochemistry of HgX_2P_2 in the presence of phosphine.

(b) Ligand-Exchange Reactions. The fact that eq 1 is an electrochemically reversible electrode process implies that the halides and phosphines are kinetically labile on the electrochemical time scale when coordinated to mercury(II). While the observation of electrochemical and chemical reversibility preclude mechanistic interpretation of pathways and intermediates associated with the electrode process, polarographic data enable the conclusion to be drawn that any equilibria of the type

$$HgX_2P_2 \rightleftharpoons HgXP_2^+ + X^- \qquad (6)$$

$$HgX_2P_2 \rightleftharpoons HgX_2P + P \qquad (7)$$

lie substantially to the left in dichloromethane. Other conclusions can also be reached. For example, the kinetically labile nature of the ligands should enable electrochemical observation of exchange reactions; this data should be consistent with that form NMR studies.

When mixtures of complexes containing the same phosphine but different halides are reduced, a single differential-pulse polarogram is observed midway between those of the individual components (Figure 3). The peak potential shows the same concentration dependence as the individual components, and the peak current is the sum of the components measured individually. Clearly rapid exchange of halides between complexes occurs in the bulk of solution so that only a single reduction peak corresponding to the time average of the individual components is observed. This is equivalent to a reaction of the type

$$HgX'_2P_2 + HgX_2P_2 \rightleftharpoons 2HgXX'P_2 \qquad (8)$$

Theoretical calculations have shown that a mixture of two nonexchanging HgX_2P_2 complexes whose individual currents simply add produces a sufficiently distorted differential-pulse polarogram to permit the mixture to be distinguished from the single, undistorted polarogram expected if the complexes undergo rapid ligand exchange if the $E_{1/2}$ values of each component differ by more than 40 mV.[20] This condition is met in 8 of the 12 mixtures examined. As shown in Table III, the observed $E_{1/2}$ values are in good agreement with the calculated from the mean of the $E_{1/2}$ values of the components. Furthermore, identical results are obtained by mixing the complex with the appropriate free halide. For example, an $E_{1/2}$ of −0.492 V was observed for the reduction of a 5.34 × 10^{-4} M solution of $HgBr_2(PBu_3)_2$ containing 10.87 × 10^{-4} M *n*-Bu_4NI; this corresponds to an $E_{1/2}$ of −0.516 V at 1.0 × 10^{-3} M which is in excellent agreement with the value cited in Table III for the $HgBr_2(PBu_3)_2$ and $HgI_2(PBu_3)_2$ mixture.

Table III. Half-Wave Potentials of Mixtures of Complexes

	$E_{1/2}$,[a] V	
mixture	obsd	calcd
$HgCl_2(PBu_3)_2$ + $HgBr_2(PBu_3)_2$	−0.473	−0.470
$HgCl_2(PBu_3)_2$ + $HgI_2(PBu_3)_2$	−0.504	−0.506
$HgBr_2(PBu_3)_2$ + $HgI_2(PBu_3)_2$	−0.510	−0.519
$HgCl_2(PPh_3)_2$ + $HgBr_2(PPh_3)_2$	−0.224	−0.222
$HgCl_2(PPh_3)_2$ + $HgI_2(PPh_3)_2$	−0.264	−0.262
$HgBr_2(PPh_3)_2$ + $HgI_2(PPh_3)_2$	−0.269	−0.273
$HgCl_2(pmp)$ + $HgBr_2(pmp)_2$	−0.302	−0.302
$HgCl_2(pmp)_2$ + $HgI_2(pmp)_2$	−0.318	−0.314
$HgBr_2(pmp)_2$ + $HgI_2(pmp)_2$	−0.326	−0.325

[a] Adjusted via eq 3 to 1.00 mM.

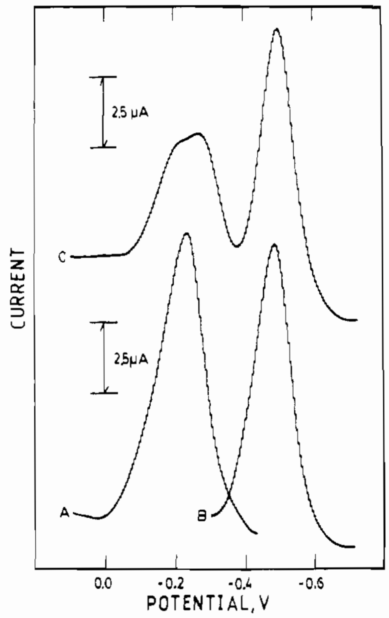

Figure 4. Differential-pulse polarographic reduction of $HgBr_2(PBu_3)_2$ + $HgBr_2(PPh_3)_2$ in dichloromethane (0.1 M Bu_4NClO_4): A, 5.35 × 10^{-4} M $HgBr_2(PPh_3)_2$; B, 5.34 × 10^{-4} M $HgBr_2(PBu_3)_2$; C, 5.35 × 10^{-4} M $HgBr_2(PPh_3)_2$ + 5.34 × 10^{-4} M $HgBr_2(PBu_3)_2$. Pulse amplitude is −50 mV, drop time is 1.0 s, and temperature is 20 °C.

Mixtures of complexes containing the same halide but different phosphines (Figure 4) show very different behavior to the variable halide experiments, implying that exchange of phosphine ligands (eq 9) in the bulk of solution does not occur

$$HgX_2P_2 + HgX_2P'_2 \rightleftharpoons 2HgX_2PP' \qquad (9)$$

to a measurable extent at room temperature over a period of several hours. The shape of the peak for the most easily reduced component appears to consist of two peaks in the example shown while that of the more difficultly reduced component retains its shape but is shifted to a slightly more negative potential. This behavior must in part result from cross-redox reactions similar to those responsible for the effects

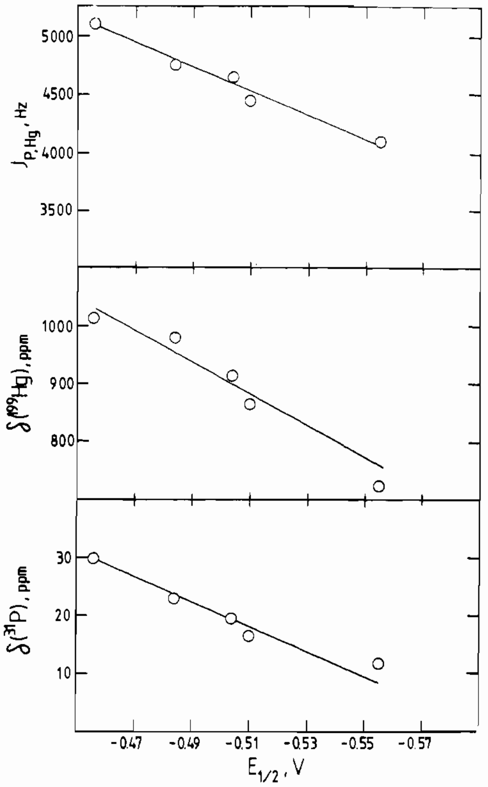

Figure 5. Comparison of ^{31}P and ^{199}Hg NMR parameters with $E_{1/2}$ for $HgX_2(PBu_3)_2$ and $HgXX'(PBu_3)_2$. NMR data are taken from ref 16.

of free halide on the reduction of the complex. For example, if HgX_2P_2 is easier to reduce than $HgX_2P'_2$

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

$$2X^- + Hg \rightleftharpoons HgX_2 + 2e^- \qquad (11)$$

$$HgX_2P'_2 + HgX_2 \rightleftharpoons Hg_2X_4P'_2 \qquad (12)$$

The quantity of HgX_2 produced is governed by the concentration of halide produced at the electrode surface during the reduction of HgX_2P_2, the applied potential, and the thermodynamic constraints of the Nernst equation.

In addition, previous data demonstrates that the exchange reaction eq 13 should also occur at the electrode surface.

$$HgX_2P'_2 + P \rightleftharpoons HgX_2P'_2P \qquad (13)$$

The three possible combinations of $HgBr_2P_2$ complexes were examined over the temperature range 20 to −30 °C. Both the type of *i–E* curve distortion observed and the effect of temperature on polarograms depended on the specific complex mixture. Complete elucidation of the electrochemistry of these mixtures will require significant advances in both electrochemical theory and the solution chemistry of HgX_2P_2 and related compounds. However, results certainly imply that NMR data[17] need further consideration (see below).

(c) Correlations with ^{199}Hg and ^{31}P NMR Data. Figures 5–7 provide plots of $E_{1/2}$ for a given concentration of HgX_2P_2 vs. the ^{199}Hg and ^{31}P chemical shift and $J_{P,Hg}$ coupling constants, respectively. An excellent correlation is observed, particularly with the $J_{P,Hg}$ NMR values. Thermodynamic considerations apply to the electrochemical data and the same phenomena appear to influence the NMR for this particular series of complexes.

Comparison of the NMR and electrochemistry with respect to exchange reactions is extremely interesting. Colton and Dakternieks[16] have shown that mixing equimolar amounts of $HgBr_2(PBu_3)_2$ and $HgI_2(PBu_3)_2$ at 30 °C in dichloromethane gives a single ^{31}P resonance whose position and coupling constant to ^{199}Hg is the average of the initial components. Similarly, only one triplet is observed in the ^{199}Hg NMR spectrum. Addition of a further quantity of $HgI_2(PBu_3)_2$ still gives only one ^{31}P resonance, but the position and coupling constant change to values closer to those of the pure iodo complex. At −120 °C, the ^{31}P NMR spectrum of the equimolar mixture consists of three resonances of approximately 1:2:1 intensities with the appropriate ^{199}Hg satellites. The two outermost peaks were identified by position and coupling constant as arising from $HgBr_2(PBu_3)_2$ and $HgI_2(PBu_3)_2$. The central peak of greatest intensity had a chemical shift and

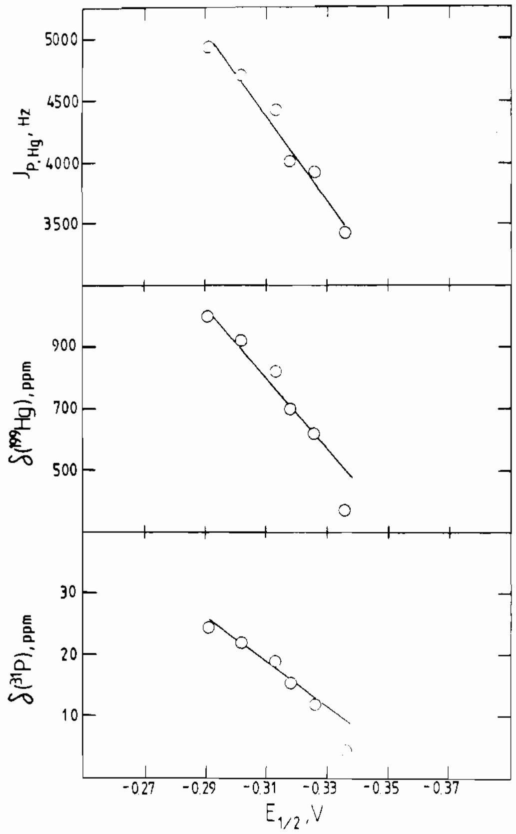

Figure 6. Comparison of ^{31}P and ^{199}Hg NMR parameters with $E_{1/2}$ for $HgX_2(pmp)_2$ and $HgXX'(pmp)_2$. NMR data are taken from ref 17.

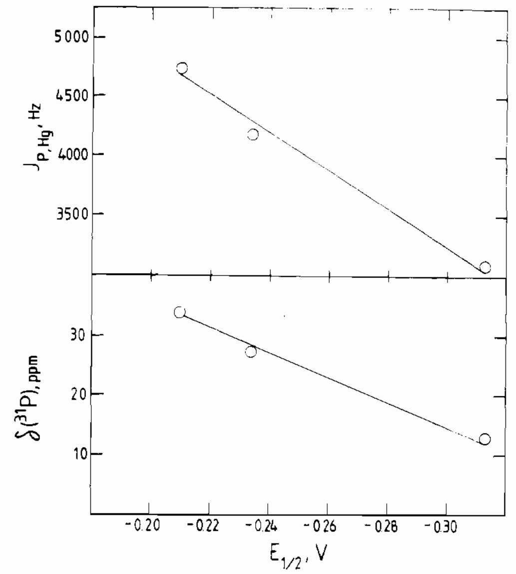

Figure 7. Comparison of $\delta(^{31}P)$ and J_{P-Hg} NMR parameters with $E_{1/2}$ for $HgX_2(PPh_3)_2$. NMR data are taken from ref 11.

coupling constant consistent with the mixed-halide complex $HgBrI(PBu_3)_2$. It was deduced from these NMR experiments that the halide complexes undergo a typical Calingaert redistribution reaction.[24]

$$HgBr_2(PBu_3)_2 + HgI_2(PBu_3)_2 \rightleftharpoons 2HgBrI(PBu_3)_2 \qquad (14)$$

Similar deductions are readily made from the electrochemical data (see eq 8). Halide-exchange reactions are observed to be extremely rapid from the NMR data which is consistent with all the electrochemical results which are characterized by reversible behavior and rapid exchange reactions involving X^- or HgX_2. NMR and other studies on HgX_2[26] demonstrate the halide lability associated with these compounds. Mixtures of HgX_2 and HgX'_2 are known to be in equilibrium with their respective mixed species:

$$HgCl_2 + HgI_2 \rightleftharpoons 2HgClI \qquad (15)$$

The same appears to be true of all related reactions such as

$$HgX_2 + HgX_2P_2 \rightleftharpoons Hg_2X_4P_2 \qquad (16)$$

as required to interpret the electrochemical data.

In NMR experiments,[17] solutions of equimolar mixtures of $HgCl_2(PBu_3)_2$ and $HgCl_2(pmp)_2$ at room temperature showed two ^{31}P resonances with mercury satellites. The coupling constants were very similar to those of the starting materials although both resonances had moved toward each other. Two resonances in the mercury spectrum confirm that at room temperature there is no appreciable concentration of the mixed-ligand complex. At lower temperatures NMR resonances attributed to $HgCl_2(PBu_3)(pmp)$ were reported. From electrochemical data, the redistribution reaction eq 17 in its

$$HgCl_2(PBu_3)_2 + HgCl_2(pmp)_2 \rightleftharpoons 2HgCl_2(PBu_3)(pmp) \qquad (17)$$

own right does not explain the exchange reaction occurring in this system. Our electrochemical results indicate that the mixtures containing different phosphine ligands require far more detailed investigation in order to provide a definitive account of the chemistry.

The available data are consistent with the fact that the mercury–halogen bond is weaker in the $HgX_2(PBu_3)_2$ complexes than in the $HgX_2(pmp)_2$ systems, while all the evidence suggests that the converse is true of the mercury–phosphorus bonds. Facile exchange reactions of the kind

$$HgX_2(pmp)_2 + HgX_2(PBu_3)_2 \rightleftharpoons [HgX_3]^- + [HgX(pmp)_2(PBu_3)_2] \qquad (18)$$

$$HgX_2(pmp)_2 + HgX_2(PBu_3)_2 \rightleftharpoons [HgX_3(PBu_3)]^- + [HgX(PBu_3)_2(PPh_3)]^+ \qquad (19)$$

in addition to other reactions would therefore be consistent with the electrochemical data at room temperature and partially account for the NMR data of the mixture not being exactly in agreement with the individually prepared solution with respect to the position of the HgX_2P_2 resonances. Presumably lower temperatures favor the reaction in eq 17 in preference to the reaction represented by eq 18 or 19. At this point in time it is clear that NMR data is inadequate for a complete understanding of the intricate range of equilibria and exchange reactions that can occur. Both electrochemical and NMR experiments indicate how facile the reactions between X^-, HgX_2, HgX_2P_2, $Hg_2X_4P_2$, etc. are. From the synthetic point of view, the system adjusts rapidly to its equilibrium position upon addition of any one of the compounds involved in the equilibrium.

In summary, the above examples demonstrate that under appropriate circumstances electrochemical techniques can provide a powerful approach to obtaining data of the kind widely obtained from NMR measurements. Work in these laboratories is continuing to develop a theory enabling a more quantitative approach to interpreting the data and to further investigation of the possible usefulness of the electrochemical approach.

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Registry No. $HgCl_2(PBu_3)_2$, 41665-91-2; $HgBr_2(PBu_3)_2$, 20968-25-6; $HgI_2(PBu_3)_2$, 41665-93-4; $HgCl_2(PPh_3)_2$, 14494-85-0; $HgBr_2(PPh_3)_2$, 14586-76-6; $HgI_2(PPh_3)_2$, 14494-95-2; $HgCl_2(pmp)_2$, 74039-80-8; $HgBr_2(pmp)_2$, 75101-22-3; $HgI_2(pmp)_2$, 75101-23-4; $(C_2H_5)_4NCl$, 56-34-8; $(C_4H_9)_4NBr$, 1643-19-2; $(C_4H_9)_4NI$, 311-28-4.

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Kinetics and Mechanism of the Reaction of Aqueous Europium(II) Ion with Pyruvic Acid

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Eu^{II} ion reacts with pyruvic acid in air-free, aqueous, acidic solutions. The only organic product is lactic acid, which forms after a two-electron reduction of the keto form of pyruvic acid. The overall stoichiometry is 2:1, metal ion to organic acid, respectively. The kinetics were studied in detail by the stopped-flow technique. Under conditions of excess Eu^{II} ion over pyruvic acid, two stages are observed: a fast stage, which corresponds to the reduction of all available keto form in equilibrium with the hydro form of pyruvic acid, and a slow stage, during which hydrated pyruvic acid reacts only after being transformed to the carbonyl form by an acid-catalyzed reaction, which under these conditions is the rate-determining step. A mechanism is proposed and compared to the mechanisms of the corresponding reactions of the d elements Cr^{2+}, V^{2+}, and Ti^{3+}.

Introduction

In view of the biological importance of the hydrogenation of pyruvic and other keto acids, we decided to undertake an investigation of their redox behavior, using low-valent metal ions as probes. This is the third paper of the series and deals with the reduction of pyruvic acid by the f-electron donor Eu^{2+}. The first two papers dealt with the reduction of pyruvic acid by the d-electron donors Cr^{2+}[1] and V^{2+}[2] ions. In using low-

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