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Electrochemical Generation of Soluble and Reactive Cadmium, Lead, and Thallium Cations in Noncoordinating Solvents: Relative Strengths of Perchlorate, Tetrafluoroborate, and Hexafluorophosphate Ligation in Dichloromethane and Benzene

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Abstract: Electrochemical oxidation of metal amalgam electrodes in noncoordinating solvents generates soluble forms of highly active metal ions at the electrode surface that can form very strong complexes with the tetrafluoroborate and perchlorate anions. Oxidation at Cd, Pb, and Tl dropping mercury amalgam electrodes in a solution containing dichloromethane and either tetrabutylammonium hexafluorophosphate, $[NBu_4][PF_6]$, tetrabutylammonium tetrafluoroborate, $[NBu_4][BF_4]$, or tetrabutylammonium perchlorate, $[NBu_4][ClO_4]$, occurs reversibly, thereby allowing thermodynamic data to be obtained on the nature of the complex formed. The $[PF_6]^-$ ligation is considerably weaker than that of $[ClO_4]^-$ or $[BF_4]^-$. Data obtained in dichloromethane with hexafluorophosphate as a reference electrolyte allowed the following complexes with their equilibrium constants to be identified: $[Cd(ClO_4)_4]^{2-}$, $\log \beta_4 = 9.1$; $[Cd(BF_4)_3]^-$, $\log \beta_3 = 7.3$; $[Pb(ClO_4)_3]^-$, $\log \beta_3 = 8.3$; $Pb(BF_4)_2$, $\log \beta_2 = 7.5$; $Tl(ClO_4)$, $\log \beta_1 = 3.3$; $Tl(BF_4)$, $\log \beta_1 = 2.9$. The equilibrium constants for these complexes are larger than those obtained in aqueous media for many classical ligands. In benzene, which is of lower dielectric constant and is less polar than dichloromethane, the half-wave potential for the oxidation of the cadmium amalgam electrode is approximately 700 mV more negative with perchlorate than with hexafluorophosphate as the electrolyte anion. In contrast, the difference is only 200 mV in dichloromethane. This unprecedented difference may be attributed to the weaker coordination of benzene and the consequent amplification of the differences in strength of perchlorate and hexafluorophosphate ligation. Consequently, a method of preparing highly activated and previously unknown forms of soluble metal ions is available in solvents such as chlorinated and aromatic hydrocarbons. This feature is further illustrated by the large negative shift in half-wave potential for the metal oxidations observed after the coordinating solvent dimethyl sulfoxide is added to dichloromethane (0.2 M $[NBu_4][PF_6]$) solutions. Controlled-potential electrolysis experiments at a mercury amalgam pool in dichloromethane lead to the formation of the expected nonsolvated insoluble salts, demonstrating that the kinetics of precipitation are slower than the polarographic time scale. Concepts developed in this work provide prospects for new forms of mechanistic, thermodynamic, and synthetic metal ion chemistry.

The study of metal ions in aqueous solution has been very extensive.[1a-c] Spectroscopic methods such as nuclear magnetic resonance and Raman spectroscopy have demonstrated that metal ions exist as strongly coordinated species of the kind $[M(H_2O)_x]^{n+}$.[2] In coordinating organic solvents similar complexes of the type $[MS_x]^{n+}$ (S = solvent) have been observed,[3] with the anions present in these studies being assumed to be noncoordinating. Initially, nitrate was used[4a,b] as a noncomplexing ion, but this has now been shown to be a coordinating ligand with many metals.[5] Recent studies[6a,b] have focussed on anions such as $[ClO_4]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, and $[PF_6]^-$, which have generally been verified to be noncoordinating except in special situations.[7a-d]

Solvated forms of metal ions $[MS_x]^{n+}$ cannot be expected to be as reactive as the noncoordinated cation M^{n+} since the free energy of the metal ion has been lowered by the reaction given in eq 1. The energetics of formation of $[M(S)_x]^{n+}$ are described

$$M^{n+} + xS \overset{K}{\rightleftharpoons} [MS_x]^{n+} \qquad (1)$$

by the classic Born–Haber cycle.[8a,b] In principle, noncoordinating solvents should enable studies to be undertaken on nonsolvated M^{n+} metal cations by dissolution of their metal salts. However, in the vast majority of cases, the salts of noncoordinating anions are insoluble in such solvents, which generally have low dielectric constants. Consequently, virtually no solution data of soluble forms of simple metal salts are available in noncoordinating media, e.g. hydrocarbons, aromatic hydrocarbons, and halogenated hydrocarbons.

In this work the possibility of electrochemically generating M^{n+} in dichloromethane and benzene has been examined. Electrochemical oxidation of a metal electrode in the presence of noncoordinating solvent and electrolyte, $[A^+][B^-]$, is expected to occur by reactions 2a–c. Equations 2a and 2b are expected to occur

$$M \rightleftharpoons M^{n+} + ne^- \qquad (2a)$$

$$M^{n+} + yB^- \rightleftharpoons [MB_y]^{(y-n)-} \qquad (2b)$$

$$[MB_y]^{(y-n)-} \xrightarrow{k_1} MB_n\downarrow + (y-n)B^- \qquad (2c)$$

at a diffusion-controlled rate, so that if the rate constant for precipitation, k_1, is slower than the electrochemical time scale, electrochemical measurements will provide thermodynamic data

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on the soluble species M^{n+} and $[MB_y]^{(y-n)-}$. That is, even if $[B]^-$ is classically regarded as a noncoordinating ligand that usually participates only in ion-pair formation, under the special conditions described above, it is predicted than an unusually ligated metal ion will be formed.

Thermodynamic descriptions of electrochemical oxidation of a pure metal electrode are often complicated by surface phenomena.[9] However, it has been demonstrated that oxidation of certain metal amalgams is usually well-defined.[10] In particular, theoretical descriptions for the dropping amalgam electrode (DAE) have been presented, and complex ion studies undertaken in coordinating solvents using these theories are available.[11a,b] In the present paper, detailed studies of the oxidation of Cd, Pb, and Tl at a DAE have been undertaken in dichloromethane in the presence of $[NBu_4][D]$ (D = $[ClO_4]^-$, $[BF_4]^-$, and $[PF_6]^-$) to examine the interaction of these anions with M^{n+} in dichloromethane. The oxidation of a Cd amalgam electrode in benzene with tetrahexylammonium perchlorate, $[NHx_4][ClO_4]$, and tetrahexylammonium hexafluorophosphate, $[NHx_4][PF_6]$, as the electrolytes is also presented to establish the generality of the proposed method for obtaining data on highly activated forms of metal ions. Finally, addition of the coordinating solvent, dimethyl sulfoxide, to dichloromethane solutions and measurement of the change in half-wave potential, $E_{1/2}$, is used to demonstrate the highly activated nature of the metal ions formed in dichloromethane.

Experimental Section

All voltammetric electrochemical experiments were undertaken with a Princeton Applied Research (PAR) 174 A polarographic analyzer. Controlled-potential electrolysis (CPE) experiments were performed with a PAR Model 173 potentiostat combined with a PAR 179 digital coulometer. The reference electrode was Ag/AgCl (dichloromethane saturated with LiCl and containing 0.1 M $[NBu_4][ClO_4]$). However, potentials from voltammetric studies are reported relative to the cobaltocene/cobaltocenium ($CoCp_2/[CoCp_2]^+$) couple. To all solutions was added 10^{-3} M $CoCp_2$ at the end of each experiment, and the voltammogram for the $CoCp/[CoCp_2]^+$ couple was recorded. Shifts in $E_{1/2}$ versus Ag/AgCl for a given series of experiments are essentially the same as those quoted versus $CoCp_2/[CoCp_2]^+$ although the absolute values of both potentials are considerably different. Ferrocene, which is a more common internal standard,[12] could not be employed because the metal oxidation interfered with the ferrocene/ferrocenium ($FeCp_2/[FeCp_2]^+$) process. The auxiliary electrode for voltammetric studies was a Pt wire and for CPE a Pt gauze separated from the cell solution by a Vycor frit. Amalgams (ca. 0.5 mM) of Cd, Pb, and Tl were prepared by dissolving weighed amounts of the respective metal in mercury. The metal surfaces were cleaned with nitric acid prior to use. The oxidation of Cd, Pb, and Tl amalgam electrode was studied by dc polarography at a DAE (droptime 0.5 s) and by cyclic voltammetry at a slowly growing amalgam drop electrode. CPE oxidation experiments were carried out with a mercury pool electrode to which a concentrated metal amalgam was slowly added during electrolysis. The oxidations in dichloromethane were undertaken in 0.2 M solutions containing either pure $[NBu_4][ClO_4]$, $[NBu_4][BF_4]$, or $[NBu_4][PF_6]$ electrolyte and in constant cation concentration (0.2 M) solutions of $[NBu_4][PF_6]/[NBu_4][BF_4]$ and $[NBu_4][PF_6]/[NBu_4][ClO_4]$ mixed electrolytes. Experiments involving dimethyl sulfoxide were undertaken by addition of dried solvent to dichloromethane (0.2 M $[NBu_4][PF_6]$). Experiments in benzene were undertaken in the presence of 0.2 M $[NHx_4][ClO_4]$ and $[NHx_4][PF_6]$ electrolytes.

Dichloromethane was dried over CaH_2 and distilled prior to use.[13] Benzene was dried over sodium and distilled prior to use. In order to minimize contamination by water, freshly activated alumina was maintained in the voltammetric cell, during all experiments. The water concentration needs to be kept as low as possible, as in solvents with very low donor properties, like dichloromethane and benzene, the influence of small amounts of water may be large. Electrolytes containing $[NBu_4]^+$ were obtained from Southwestern Analytical Chemicals. $[NHx_4][ClO_4]$ was obtained from GFS Chemicals, and $[NHx_4][PF_6]$ was made by reaction of $[NHx_4]I$ and KPF_6. Electrolytes containing perchlorate were purified by dissolving in CH_2Cl_2, stirring over sodium sulfate, filtering, and then precipitating the electrolyte by addition of diethyl ether. The resulting precipitate was isolated by filtration and dried in vacuo. $[NBu_4][BF_4]$ and $[NBu_4][PF_6]$ were dissolved in CH_2Cl_2, and the solution was stirred over sodium sulfate, filtered, and evaporated to dryness. The resulting solid was dried in vacuo. Cobaltocene was obtained from ICN Biomedicals and triply distilled mercury from Engelhard Industries; both of these reagents were used as received.

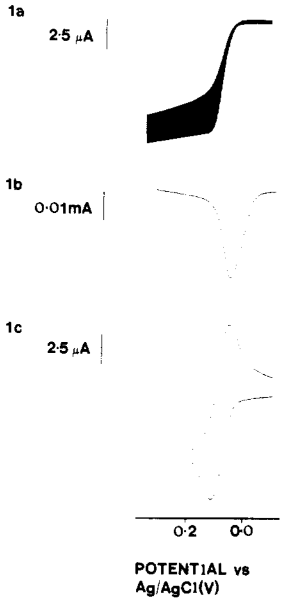

Figure 1. Voltammetric curves for the oxidation of a lead mercury amalgam electrode in dichloromethane containing 0.2 M $[NBu_4][ClO_4]$: (a) dc polarogram, (b) differential-pulse polarogram, (c) cyclic voltammogram.

All solutions were purged with solvent-saturated argon to remove oxygen. Data are reported at 22 ± 1 °C. CPE of a Cd amalgam pool in dichloromethane solution containing 0.2 M $[NBu_4][BF_4]$ produces a cream precipitate, which was isolated by filtration, washed with CH_2Cl_2 to remove base electrolyte, and dried in vacuo. The resultant material is hydroscopic. Anal. Calcd for $Cd(BF_4)_2$: Cd, 39.3. Found: Cd, 39.6. The cadmium analysis was performed by polarographic methods at a dropping mercury electrode. Standard additions of dried cadmium carbonate and the unknown were made to an aqueous solution of 0.1 M $NaClO_4$.

Results and Discussion

Figure 1 shows typical oxidative dc polarograms, differential-pulse polarograms, and cyclic voltammograms obtained at a Pb amalgam dropping electrode in a solution of dichloromethane containing 0.2 M $[NBu_4][ClO_4]$. Similar quality data were obtained for the other metals provided the metal amalgam concentration was less than 0.5 mM. At higher amalgam concentrations, maxima, erratic responses, and irregular drop formation were observed. For the dilute amalgams, plots of E versus log $(i_d/(i - i_d))$[14] were close to the theoretically expected values (29 mV (Cd, Pb) and 58 mV (Tl)) for a soluble product; that is, the reactions are as shown in eq 3a and 3b.

$$M(Hg) \rightleftharpoons M^{2+}(sol) + Hg + 2e^- \qquad M = Cd, Pb \tag{3a}$$

$$Tl(Hg) \rightleftharpoons Tl^{+}(sol) + Hg + e^- \tag{3b}$$

If an insoluble product had resulted, then a different response would have been theoretically predicted. It is possible that nucleation and precipitation reactions cause the erratic behavior at high amalgam concentrations, but importantly the kinetics of precipitation must be sufficiently slow so as not to influence the

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[14] $E_{1/2}^{rev}$ is the reversible electrode half-wave potential, i_d is the diffusion-controlled limiting current, and i is the current at potential E.

Table I. Oxidation Half-Wave Potentials of Cd, Pb, and Tl (Amalgam) Electrodes in Dichloromethane[a]

		dc polarography (drop time 0.5 s)		cyclic voltammetry (scan rate 500 mV s^{-1})			differential-pulse polarography (pulse width 50 ms)	
metal	electrolyte[b]	$E_{1/2}{}^{c}/V$	$E_{3/4} - E_{1/4}/V$	$E_p{}^{ox}/V$	$\Delta E_p/V$	$E_{1/2}{}^{c,d}/V$	$E_{1/2}{}^{c,e}/V$	$W_{1/2}/V$
cadmium	$[NBu_4][PF_6]$	1.07	0.03	1.13	0.12	1.07	1.08	0.07
	$[NBu_4][ClO_4]$	0.89	0.03	0.90	0.04	0.88	0.88	0.08
	$[NBu_4][BF_4]$	0.88	0.03	0.95	0.10	0.89	0.90	0.08
lead	$[NBu_4][PF_6]$	1.17	0.03	1.21	0.03	1.18	1.18	0.08
	$[NBu_4][ClO_4]$	0.97	0.03	1.00	0.04	0.98	0.98	0.07
	$[NBu_4][BF_4]$	0.98	0.03	1.03	0.11	0.97	1.01	0.10
thallium	$[NBu_4][PF_6]$	0.91	0.06	0.95	0.07	0.91	0.91	0.15
	$[NBu_4][ClO_4]$	0.77	0.06	0.80	0.07	0.76	0.77	0.17
	$[NBu_4][BF_4]$	0.78	0.05	0.84	0.08	0.80	0.79	0.15

[a] $E_{1/2}$ = half-wave potential; $E_{3/4}$ and $E_{1/4}$ = potential at three-fourths and one-fourth of wave height, respectively; $E_p{}^{ox}$ = oxidation peak potential; $E_p{}^{red}$ = reduction peak potential; ΔE_p = separation in peak potential; $W_{1/2}$ = width at half-wave height. [b] Electrolyte concentration 0.2 M. [c] Potentials quoted with respect to $CoCp_2/[CoCp_2]^+$ couple. [d] Calculated from the relationship $(E_p{}^{ox} + E_p{}^{red})/2$. [e] Calculated from the relationship $(E_p + \Delta E/2)$, where ΔE = pulse amplitude.

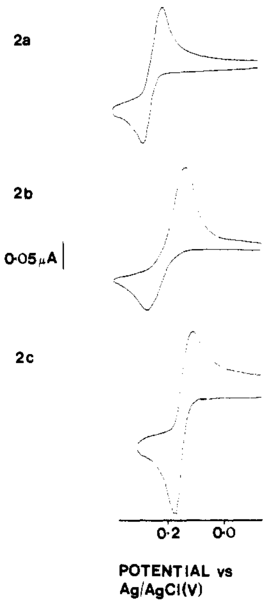

Figure 2. Cyclic voltammograms for the oxidation of a cadmium mercury amalgam electrode in dichloromethane containing (a) 0.2 M $[NBu_4][PF_6]$, (b) 0.1 M $[NBu_4][PF_6]$ and 0.1 M $[NBu_4][BF_4]$, and (c) 0.2 M $[NBu_4][BF_4]$.

result under conditions where the amalgam is dilute.

The CPE product obtained from the oxidation of Cd in the presence of $[BF_4]^-$ establishes that a nonsolvated neutral salt is the final product of the metal oxidation. In contrast, a soluble product is formed at the electrode surface on the polarographic time scale. These observations suggest that precipitation occurs on the seconds time scale. Some evidence for precipitation on the voltammetric time scale may be seen in the particular case of Cd oxidized in a solution containing dichloromethane and an equimolar mixture of 0.1 M $[NBu_4][BF_4]$ and 0.1 M $[NBu_4][PF_6]$ (Figure 2). The more symmetrical curve shape of the cyclic voltammogram suggests adsorption (precipitation) occurs. Equivalent evidence for precipitation is seen in dc polarography and differential-pulse curves.

The data obtained from dc polarography, differential-pulse polarography, and cyclic voltammetry are shown in Table I. Calculated reversible half-wave potential ($E_{1/2}{}^{rev}$) values are closely related to the standard redox potential ($E°$) for the reaction shown in eq 4. The three techniques used to calculate $E_{1/2}{}^{rev}$ have

$$M(Hg) \rightleftharpoons M^{n+}(sol) + ne^- + Hg \tag{4}$$

distinctly different time domains (dc polarography drop time, 0.5 s; cyclic voltammetric scan rate, 500 mV s^{-1}; differential-pulse polarography pulse width, 50 ms). The fact that results are technique and time independent supports the concept that thermodynamically valid data are being obtained. Assuming the use of $CoCp_2/[CoCp]_2{}^+$ as a reference redox couple eliminates junction potentials, then the conclusion is reached that $E_{1/2}{}^{rev}$ is considerably less negative when $[NBu_4][PF_6]$ is used as the electrolyte than when $[NBu_4][ClO_4]$ and $[NBu_4][BF_4]$ are used. The difference in potential relative to $[NBu_4][PF_6]$ is metal dependent but lies in the range 100–200 mV. One possible explanation of this would be different strengths of ion-pair formation. However, the differences in $E_{1/2}{}^{rev}$ observed appear to be far too large to be accounted for by variation in ion-pair strength between anions that are all singly charged and of similar size. The trend with respect to metal is also inconsistent with an ion-pair explanation. The variation in $E_{1/2}{}^{rev}$, with the different anions, therefore must arise from terms additional to simple electrostatic ones.

One possible interpretation is that $[ClO_4]^-$ and $[BF_4]^-$ anions are acting as strong ligands relative to $[PF_6]^-$. Many complexes of $[BF_4]^-$ and $[ClO_4]^-$ have been reported but not usually in situations where these are the only ligands. If the assumption is made that $[PF_6]^-$ is noncoordinating, then the shift in $E_{1/2}{}^{rev}$ in mixtures of $[NBu_4][PF_6]/[NBu_4][ClO_4]$ and $[NBu_4][PF_6]/[NBu_4][BF_4]$ at constant cation concentration should provide information on the nature and stability of the complexes formed, assuming that all electrolytes are completely dissociated. In low dielectric constant media, some ion pairing will occur, so that the concentration of free anion has some uncertainty. Data were obtained at a nominal ionic strength of 0.2 M. Under these conditions, as the concentration of $[ClO_4]^-$ or $[BF_4]^-$ increases, $E_{1/2}{}^{rev}$ becomes more negative. If only one complex is formed with an equilibrium constant β_g for the reaction shown in eq 5, then

$$M^{n+} + gX^- \overset{\beta_g}{\rightleftharpoons} [MX_g]^{(n-g)+} \tag{5}$$

β_g is related to $E_{1/2}{}^{rev}$ by the relationship shown in eq 6, assuming

$$E_{1/2}{}^{rev}(complex) - E_{1/2}{}^{rev}(free) = \frac{-RT}{nF} \ln \beta_g - \frac{RT}{nF} \ln [X^-]^g \tag{6}$$

equal diffusion coefficients for the free and the complexed metal ions.[10,15a–c] The assumption of equal diffusion coefficients is considered to be an excellent approximation since the limiting current of dc polarograms was almost electrolyte and electrolyte concentration independent. A further assumption made is that the concentration of $[X^-]$ is the analytical concentration. Under conditions where the anion concentration is in a considerable excess over the metal concentration in the amalgam and ion pairing is negligible, this assumption is valid. From eq 6 it follows that a plot of $(E_{1/2}(complex) - E_{1/2}{}^{rev}(free))$ versus ln [anion] should be linear and of slope $-gRT/nF$ and intercept $(-RT/nF) \ln \beta_g$.

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Table II. Coordination Numbers and Equilibrium Constants for Cd, Pb, and Tl Complexes with Weak Ligands

metal	anion	solvent	coordn no. (n)	log β_n	ref
Cd	$[ClO_4]^-$	CH_2Cl_2	4^a	9.1	this work
	$[BF_4]^-$	CH_2Cl_2	3^a	7.3	this work
	Cl^-	H_2O	4	1.6	16
			3	1.5	16
	Br^-	H_2O	4	2.6	16
			3	2.6	16
	I^-	H_2O	4	5.6	16
			3	4.5	16
	$[NO_3]^-$	H_2O	2	-0.8	16
Pb	$[ClO_4]^-$	CH_2Cl_2	3^a	8.3	this work
	$[BF_4]^-$	CH_2Cl_2	2^b	7.5	this work
	Cl^-	H_2O	3	1.4	16
			2	1.3	16
	Br^-	H_2O	3	2.2	16
			2	1.8	16
	I^-	H_2O	3	3.4	16
			2	2.8	16
	$[NO_3]^-$	H_2O	3	0.2	16
			2	0.4	16
Tl	$[ClO_4]^-$	CH_2Cl_2	1^a	3.3	this work
	$[BF_4]^-$	CH_2Cl_2	1^a	2.9	this work
	Cl^-	H_2O	1	0.04	16
	Br^-	H_2O	1	0.41	16
	I^-	H_2O	1	0.74	16
	$[NO_3]^-$	H_2O	1	-0.48	16

[a] Coordination numbers obtained in this work have been rounded off to the nearest integer and have an error of ±0.2. The designated complex is the predominant species over the anion concentration range of 0.001-0.2 M. [b] Coordination number is 3 at higher anion concentrations.

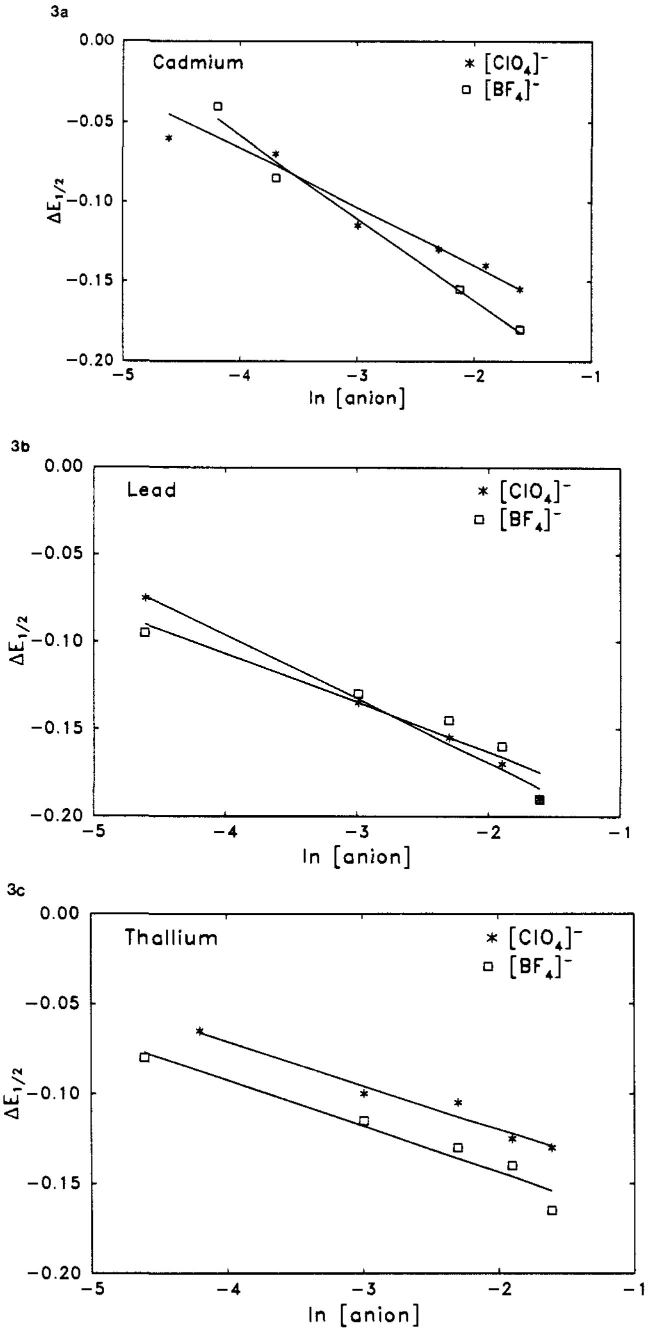

Figure 3. Graphs showing the variation of $\Delta E_{1/2}$ ($\Delta E_{1/2} = E_{1/2}^{rev}$(complex) − $E_{1/2}^{rev}$(free)) with ln [anion] (anion = $[BF_4]^-$ or $[ClO_4]^-$) for (a) cadmium, (b) lead, and (c) thallium. Lines drawn are linear least-squares fits of the data.

Plots of this kind are shown in Figure 3, while Table II summarizes the coordination number and equilibrium (overall stability) constants. The data in either pure $[NBu_4][PF_6]$, $[NBu_4][BF_4]$, or $[NBu_4][ClO_4]$ electrolytes are consistent with a completely reversible response. As indicated previously, when mixtures of electrolyte are present, some minor departures from the reversible model are evident. Consequently, $E_{1/2}$, in mixed electrolytes, does not exactly represent the thermodynamic E° value, although errors are small and have been neglected in the calculations. In view of all the assumptions inherently present in the calculations, the reported stability constants are considered to approximate values (probably a lower limit). However, other techniques are not available to obtain comparative data since they require soluble bulk solutions that cannot be obtained for these systems. In this sense the data obtained by the amalgam method are unique.

The assumption that $[PF_6]^-$ is a noncoordinating ligand leads to the conclusion that the coordinate number for thallium is unity for both $[ClO_4]^-$ and $[BF_4]^-$ as ligands. That is, the soluble complex formed is $Tl[ClO_4]$ (log $\beta_1 = 3.3$) and $Tl[BF_4]$ (log $\beta_1 = 2.9$). The equilibrium constant (log β_g) for both of the above thallium complexes in CH_2Cl_2 is of the order of 3, which indicates that the complexes are almost completely nondissociated.

In the case of lead, the coordination number is 3 for $[ClO_4]^-$ (log $\beta_3 = 8.3$) over the entire concentration range examined whereas, for $[BF_4]^-$ (log $\beta_2 = 7.5$), the data are consistent with a coordination number of 2 at low concentration and 3 at higher concentrations of the anion. The equilibrium constants found for these two lead complexes are comparable with that reported for $[Pb(OH)_3]^-$[17] in aqueous media. The data obtained at the cadmium electrode indicate the formation of $[Cd(BF_4)_3]^-$ (log $\beta_3 = 7.3$) and $[Cd(ClO_4)_4]^{2-}$ (log $\beta_4 = 9.1$). Thus, as in the case of lead, the perchlorate ion forms a higher coordination number. The value of log β_4 obtained for $[Cd(ClO_4)_4]^{2-}$ is higher than that found for the complex formed between cadmium and pyridine[18] in aqueous media, indicating the substantial strength of the complex in CH_2Cl_2.

All of the above data fit the model for formation of classic inorganic complexes, in the sense that the coordination numbers are normal for each metal ion. The data in Table II show that $[ClO_4]^-$ and $[BF_4]^-$ complexes in CH_2Cl_2 are apparently considerably stronger than those formed with many other ligands in aqueous media. However, equilibrium constants in coordinating solvents are for the reaction shown in eq 7. Thus in CH_2Cl_2 a

$$[M(S)_x]^{n+} + yL^- \rightleftharpoons [M(L)_y(S)_{x-y}]^{(n-y)+} + yS \qquad (7)$$

highly activated form of the metal ion is generated. CH_2Cl_2, if it coordinates at all, can be assumed to form only a very weak complex. The strength of the $[PF_6]^-$ complex formed with these metals, is hard to predict. However, it is clearly a much weaker ligand in CH_2Cl_2 than either $[BF_4]^-$ or $[ClO_4]^-$ by several orders of magnitude.

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In order to establish the generality of the concepts described in this paper, the oxidation of a cadmium amalgam in benzene containing 0.2 M $[NHx_4][ClO_4]$ or 0.2 M $[NHx_4][PF_6]$ was examined. Benzene has a lower dielectric constant than CH_2Cl_2 and is a nonpolar molecule. Thus, it would be expected to be even more weakly coordinating than CH_2Cl_2. With $[NHx_4][ClO_4]$ as the electrolyte, an $E_{1/2}$ value of 0.77 V was obtained versus $[CoCp_2]/[CoCp_2]^+$. This can be compared with a value of 1.45 V obtained in $[NHx_4][PF_6]$. Even in the presence of electrolyte, the benzene solution is of very high resistance, and all $E_{1/2}$ values are affected by ohmic *iR* drop. This factor precludes quantitative calculations of solution equilibria as was possible in CH_2Cl_2. However, the relative value of $E_{1/2}$ in $[ClO_4]^-$-containing electrolyte being 600–700 mV more negative than that in $[PF_6]^-$-containing electrolyte confirms that perchlorate is a much better ligand than hexafluorophosphate and that the combination of a poorly coordinating solvent, benzene, and a weak ligand $[PF_6]^-$ leads to an extremely positive $E_{1/2}$ value for the $Cd^{2+}/Cd(Hg)$ redox couple.

The above data imply that in CH_2Cl_2 and benzene a highly activated metal ion is produced. This hypothesis is further supported by experiments in which dimethyl sulfoxide (0.1 M) was added to CH_2Cl_2 containing $[NBu_4][PF_6]$ (0.2 M). Negative shifts in $E_{1/2}$ of 480, 440, and 160 mV were observed for data obtained at Cd, Pb, and Tl amalgam electrodes, respectively, versus the data obtained in CH_2Cl_2 containing $[NBu_4][PF_6]$ only (Table I). The shifts are attributable to the strong complexation of dimethyl sulfoxide relative to dichloromethane.

Summary

The electrochemical oxidation of Cd, Pb, and Tl mercury amalgam electrodes in noncoordinating media such as chlorinated or aromatic hydrocarbon solvents generates a highly activated form of the metal ion, which is strongly complexed by both $[ClO_4]^-$ and $[BF_4]^-$, anions that are normally regarded as noncoordinating ligands. Thus, if ligands can react at the electrode surface faster than the kinetics of precipitation, then a pathway to previously unknown complexes is available. The identification of soluble $[Cd(ClO_4)_4]^{2-}$, $[Cd(BF_4)_3]^-$, $[Pb(ClO_4)_3]^-$, $Pb(BF_4)_2$, $Tl(ClO_4)$, and $Tl(BF_4)$ complexes in dichloromethane is an example of new complexes as is the facile electrochemical synthesis of nonsolvated $Cd(BF_4)_2$.

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Registry No. Cd, 7440-43-9; Pb, 7439-92-1; Tl, 7440-28-0; PF_6^-, 16919-18-9; BF_4^-, 14874-70-5; ClO_4^-, 14797-73-0; Hg, 7439-97-6; CH_2Cl_2, 75-09-2; $(CH_3)_2SO$, 67-68-5; $[Cd(ClO_4)_4]^{2-}$, 104494-05-5; $[Cd(BF_4)_3]^-$, 114446-59-2; $[Pb(ClO_4)_3]^-$, 114446-60-5; $Pb(BF_4)_2$, 13814-96-5; $Tl(ClO_4)$, 13453-40-2; $Tl(BF_4)$, 28625-02-7; benzene, 71-43-2.

Simulation of Free Energy Relationships and Dynamics of S_N2 Reactions in Aqueous Solution

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Abstract: The energetics and dynamics of the S_N2 class of reactions in aqueous solution are studied by a combination of the empirical valence-bond (EVB) method and a free energy perturbation technique. The solvent is represented by the surface-constrained all-atom solvent (SCAAS) model, and many-body interactions are taken into account with a solvent parameter set that includes atomic polarizabilities. The EVB representation of the reaction conveniently incorporates the effect of the solvent reaction field on the polarization of the solute. The calculations evaluate the activation free energies for the $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ reactions and explore the general relationship between the reaction free energies (ΔG_0) and the solvent contribution to the activation free energies (Δg^{*}). The simulated free energy relationship is similar to Marcus' macroscopic formula, provided that the relevant reorganization energy is estimated from the microscopic simulation. The dynamical aspects of the S_N2 charge-transfer reaction are examined by propagating trajectories downhill from the transition state and by using the linear response theory. It is found that the rather complicated solute–solvent coupling must be included in a consistent way in order to explore the nature of the reactive trajectories. The simulations indicate that the solvent fluctuations play a major role in driving the system toward the transition state and that the relaxation time for the reactive fluctuations is determined by both the polarization time of the solute dipole moment and the dielectric relaxation time of the solvent. The characteristics of the free energy fuctionals (which are the bases for phenomenological analytical models of charge-transfer reactions) are discussed, and the suitability of studying these functionals with the EVB formulation is demonstrated.

I. Introduction

The study of chemical reactions in solution has attracted significant theoretical interest in recent years (ref 1–26 provide a partial list of works and emphasize studies of charge-transfer reactions). This interest reflects in part the realization that many

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