for 24 h. 2-Propanol (100 mL) was then added slowly to destroy unreacted alkylaluminum reagent. The solvent was then removed under reduced pressure, and the residue was extracted with methylene chloride. Triethylamine (100 mL) was added and the solution was filtered through neutral alumina. The solvent was removed, and the residue was extracted with hexane. Filtration and solvent removal yielded the product as a colorless oil which was purified by vacuum distillation.

Synthesis of $[(NPClNMe_2)_{0.6}(NP(NMe_2)_2)_{0.4}]_n$ (22). Into a solution of $(NPCl_2)_n$ (**21**) (20 g, 0.17 mol) in toluene (1200 mL) was condensed dimethylamine (35 mL, 0.53 mol) over a period of 4 h. The solution was stirred for 16 h. The precipitated dimethylamine hydrochloride was removed by filtration through a medium-frit under an atmosphere of dry argon followed by washing with additional toluene (300 mL). The combined toluene solutions were then degassed to remove unreacted dimethylamine. The final volume was 1300 mL. This solution was stored in an inert-atmosphere drybox and was used for further reactions with trimethylaluminum. Polymer **22** was isolated for characterization following removal of the toluene solvent under reduced pressure.

Synthesis of $[NP(CH_3)NMe_2)_{0.6}(NP(NMe_2)_2)_{0.4}]_n$ (23). To a solution of **22** in toluene (830 mL), prepared as described above, was added $(CH_3)_3Al$ (80 mL of a 2.0 M solution in toluene) dropwise over a period of 60 min. The polymer precipitated from solution, and stirring was continued for an additional 16 h. After this time, the reaction mixture was cooled to 0 °C and NaOH (600 mL of a 1.0 M aqueous solution) was added slowly to destroy unreacted alkylaluminum reagent. The organic and aqueous layers were decanted, and the polymer was dissolved in a mixture of THF (800 mL) and NaOH (600 mL of a 1.0 M aqueous solution). The organic layer was collected and concentrated to $\simeq$100 mL. The product was isolated following centrifugation. Purification by reprecipitation (3×) from THF into water yielded 10.1 g of **23**.

Acknowledgment. This work was supported by the Office of Naval Research. We thank Ethyl Corp. for a gift of hexachlorocyclotriphosphazene, D. J. Brennan for obtaining the GPC data, and J. M. Graaskamp for obtaining the DSC data.

Registry No. **2** (R = CH_3), 32997-23-2; **2** (R = C_2H_5), 112137-47-0; **3** (R = CH_3), 112069-20-2; **3** (R = C_2H_5), 112069-21-3; **4** (R = CH_3), 71332-21-3; **4** (R = C_2H_5), 71332-23-5; **5**, 3721-13-9; **6**, 2203-74-9; **7**, 1078-85-9; **8** (R = CH_3), 66621-95-2; **8** (R = C_2H_5), 112137-46-9; **9** (R = CH_3), 112069-16-6; **9** (R = C_2H_5), 112069-17-7; **10** (R = CH_3), 112069-18-8; **10** (R = C_2H_5), 112069-19-9; **12**, 112069-25-7; **13**, 112069-26-8; **16**, 28049-39-0; **17**, 112069-22-4; **18**, 33193-09-8; **19**, 92276-63-6; **20** (R = CH_3), 112069-23-5; **20** (R = C_2H_5), 112069-24-6; **21**, 26085-02-9.

Generation of Mercury and Cadmium Cationic Complexes from Oxidation Processes Observed in the Presence of Dimethylmercury and Dimethylcadmium at Mercury, Platinum, and Glassy Carbon Electrodes

A. M. Bond* and N. M. McLachlan

Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, Victoria 3217, Australia

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Electrochemical oxidation processes at mercury, platinum, and glassy carbon electrodes in the presence of Me_2Hg generate a mercury-rich cationic complex that is believed to be $[Me_2Hg_3]^{2+}$ or a closely related species. At mercury electrodes, direct participation of the electrode is involved in the electrochemical reaction, which is postulated to occur according to $Me_2Hg + 2Hg \rightarrow [Me_2Hg_3]^{2+} + 2e^-$. Reduction of the mercury-rich cation $[Me_2Hg_3]^{2+}$ at a platinum electrode leads to deposition of elemental mercury and regeneration of Me_2Hg at the mercury-plated platinum electrode: $[Me_2Hg_3]^{2+} + 2e^- \rightarrow Me_2Hg + 2Hg$. At platinum and glassy carbon electrodes, $[Me_2Hg_3]^{2+}$ is also produced as a product of controlled potential electrolysis experiments. In this case, the initially generated $[Me_2Hg]^+$ complex is formed at very positive potentials. $[Me_2Hg]^+$ then reacts rapidly to generate the cationic methyl mercury complex. The overall process at platinum and glassy carbon electrodes is proposed as $3Me_2Hg \rightarrow [Me_2Hg_3]^{2+} + 4Me^\bullet + 2e^-$. Oxidation processes associated with the presence of Me_2Cd are also electrode-dependent. At mercury electrodes, alkyl and metal exchange occurs via a bimetallic alkylcadmium–mercury intermediate: $Me_2Cd + Hg \rightarrow Me_2Hg + Cd^{2+} + 2e^-$. At platinum and glassy carbon electrodes the reaction occurs at more positive potentials than at mercury electrodes and generates inorganic cadmium ions: $Me_2Cd \rightarrow Cd^{2+} + 2Me^\bullet + 2e^-$.

Introduction

The chemical and physical properties of alkylated mercury and cadmium compounds have been widely studied.[1,2] Dimethylcadmium is highly reactive and used in organic synthesis as a methylating reagent.[1] Dimethylmercury is far more stable and exists even in water for considerable periods of time.[3] Consequently, dimethylmercury and its more stable monomethyl derivatives are of considerable environmental importance, and their presence in marine food chains has been linked to localized poisonings of human populations.[1,3,4]

While a great deal is known about the chemical reactions and toxicity of dimethylcadmium and dimethylmercury, very little is known about their redox properties. As far

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(1) Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982.

(2) Wardell, J. L., Ed. *Organometallic Compounds of Zinc, Cadmium and Mercury*; Chapman and Hall; London, 1985.

(3) Wood, J. M. *Science* (*Washington, DC*) 1974, *183*, 1049.

(4) *Heavy Metals in the Environment, Proceedings of the 3rd International Conference*; Amsterdam 1981; C.E.P. Consultants Ltd.: Edinburgh, Scotland.

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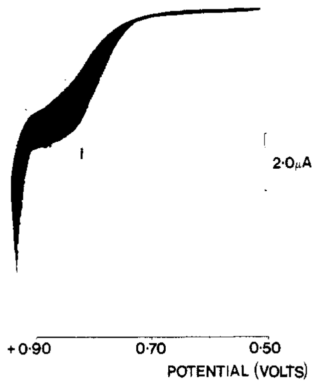

Figure 1. DC polarogram for a 6.6 × 10^{-4} M solution of Me_2Hg obtained at positive potentials in dichloromethane (0.1 M Bu_4NClO_4) at (20 ± 1) °C with a drop time of 0.5 s.

as the authors are aware, there have been no detailed reports of electrochemical studies on alkylcadmium compounds. In the case of methylethylmercury, the presence of an irreversible oxidation process was reported at very positive potentials at a platinum electrode in acetonitrile.[5] At mercury electrodes, the existence of oxidation processes in the presence of dimethyl-, diethyl-, and diphenylmercury were noted[6,7] in dichloromethane. As was the case for processes at solid electrodes, mechanistic information and product identification were not provided. Dialkylmercury compounds while capable of oxidation appear to be very difficult to reduce and are electroinactive prior to the solvent reduction in commonly used solvents. In contrast to the paucity of information on the electrochemistry of dialkylmercury compounds, the reduction of monoalkylmercury compounds has been studied in considerable detail.[8]

In this paper, detailed information on electrochemical oxidation processes associated with the presence of dimethylmercury and dimethylcadmium at platinum, glassy carbon, and mercury electrodes is presented.

Experimental Section

The techniques of direct current (DC) polarography, differential pulse polarography, controlled potential electrolysis, and cyclic voltammetry were undertaken with previously described EG & G Princeton Applied Research Corp. instrumentation.[6,7] Polarographic data at the dropping mercury electrode and voltammetric data at platinum and glassy carbon working electrodes in dichloromethane (0.1 M Bu_4NClO_4) were obtained at (20 ± 1) °C by using an Ag/AgCl (saturated LiCl, CH_2Cl_2) reference electrode and a platinum wire auxiliary electrode. Controlled potential electrolysis experiments in dichloromethane were performed at mercury pool, glassy carbon rod, and platinum basket working electrodes by using the Ag/AgCl reference electrode described above and a platinum gauze auxiliary electrode separated from the test solution by a glass frit. Voltammetric and polarographic experiments in acetonitrile (0.1 M Et_4NClO_4), acetone (0.1 M Et_4NClO_4), and water (0.1 M $NaNO_3$) were performed with an aqueous Ag/AgCl (3 M KCl) reference electrode. The analytical grade solvents and electrochemical grade electrolytes were used with drying where necessary. Dimethylmercury, dimethylcadmium, and methylmercuric chloride were used as supplied by the manufacturer (Alfa Products).

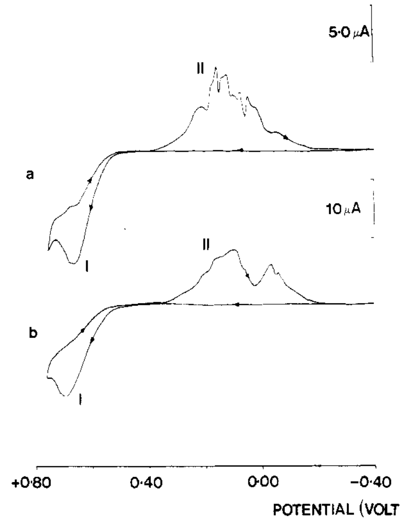

Figure 2. Cyclic voltammograms for a 6.6 × 10^{-4} M solution of Me_2Hg in dichloromethane (0.1 M Bu_4NClO_4) at (20 ± 1) °C obtained at a dropping mercury electrode. Scans at (a) 100 mV s^{-1} and (b) 200 mV s^{-1} were commenced after 0.5 s of drop growth.

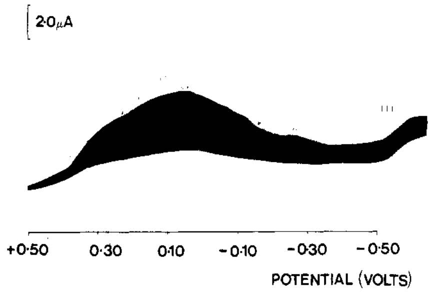

Figure 3. DC polarogram recorded after exhaustive oxidative electrolysis at a mercury pool electrode for a 6.6 × 10^{-4} M solution of Me_2Hg in dichloromethane (0.1 M Bu_4NClO_4). Other experimental parameters are as in Figure 1.

Results and Discussion

1. Oxidation Processes at Mercury Electrodes in the Presence of Dimethylmercury, Me_2Hg. In dichloromethane, a well-defined oxidation process with a half-wave potential of around 0.75 to 0.8 V vs. Ag/AgCl is observed at mercury electrodes in the presence of Me_2Hg at potentials close to the mercury electrode oxidation limit (Figure 1, process I). The DC limiting current per unit concentration, after background correction, is (1.8 ± 0.1) times that of the known one-electron reduction[8] of methylmercuric chloride (MeHgCl) when data are obtained under the same conditions. Presumably oxidation process I involves the transfer of two electrons per molecule at the dropping mercury electrode.

Figure 2 shows cyclic voltammograms recorded at 200 and 100 mV s^{-1} at a growing mercury drop electrode. The oxidation process I is chemically irreversible. On the reverse scan, a complicated and "noisy" reduction process occurs over the potential range +0.5 to −0.2 V vs Ag/AgCl (labeled process II in Figure 2). The shape of this process observed on the reverse scan is very dependent on scan rate, switching potential, drop size, and concentration. No further reduction waves are observed in cyclic voltammograms at more negative potentials on the reverse scan.

Exhaustive controlled potential electrolysis (with coulometric monitoring) in the limiting current region of process I and just prior to the onset of the mercury oxidation wave results in the transfer of 1.8 ± 0.2 electrons

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(5) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790 and references cited therein.

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(7) Bond, A. M.; McLachlan, N. M. *J. Electroanal. Chem.* **1985**, *194*, 37.

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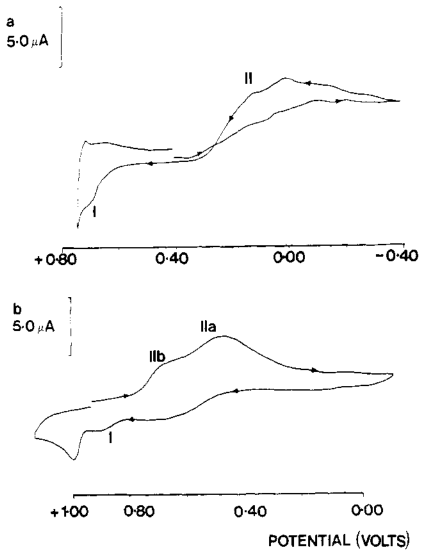

Figure 4. Cyclic voltammograms recorded at a scan rate of 200 mV s^{-1} after exhaustive oxidative electrolysis at a mercury pool electrode of process I for a 6.6 × 10^{-4} M solution of Me_2Hg in dichloromethane (0.1 M Bu_4NClO_4) obtained at (a) a dropping mercury electrode and (b) a platinum disk electrode. Appropriate experimental parameters are as in Figures 1 and 2.

per molecule. This result is consistent with the polarographic data. During the course of the electrolysis, the oxidation wave is replaced by a broad reduction response (Figure 3, process II) and a well-defined reduction process (Figure 3, process III) at more negative potentials. Process III at −0.6 V vs. Ag/AgCl is attributable to reduction of MeHgCl by comparison of the polarographic response with an authentic sample. Process II correlates with the process observed on the reverse scan of cyclic voltammograms of Me_2Hg (Figure 2). The exact shape of process II and the height of process III in Figure 3 were variable. As the height of process III increased, process II became more complex. The controlled potential electrolysis experiment is performed at potentials close to the mercury oxidation limit, and the height of process III was observed to be greater when the controlled potential was set at more positive potentials.

The DC polarogram of process II that is observed after electrolysis at a mercury pool electrode includes a large maximum. Cyclic voltammograms at mercury electrodes for process II are also complex (Figure 4a). However, on the reverse scan, Me_2Hg is observed to be a product of reduction process II. That is, the starting material can be regenerated by the oxidation–reduction cycle at mercury electrodes.

Platinum electrode voltammetry in the potential region of process II after electrolysis at a mercury pool electrode provides considerable information on the nature of the products. At a platinum electrode, process II is resolved into two processes labeled IIa and IIb (Figure 4b). The relative heights of these processes are critically dependent on the electrolysis conditions at the mercury pool electrode. Process IIa is more evident at platinum electrodes when process III is large at the DME. The platinum electrode data suggest that process II at the DME is actually two unresolved processes that are further complicated by maxima.

Voltammetric data at platinum electrodes also reveal other features when the switching potential is varied. Figure 4b is a cyclic voltammogram of the electrolyzed solution recorded at a platinum electrode by first scanning the potential in the negative direction to a switching potential just after processes IIa and IIb and then scanning in the positive potential direction to reveal the well-defined and characteristic elemental mercury stripping peak at about +1.0 V vs Ag/AgCl. These data verify that reduction process II arises from the presence of a mercury containing compound that can be reduced to elemental mercury. Furthermore, process I is observed on the reverse scan at the now mercury-coated platinum electrode that is formed by in situ deposition of mercury (Figure 4b). Formation of Me_2Hg is as expected from the cyclic voltammetric experiment at mercury electrodes (Figure 4a). Reduction process II therefore results in the generation of both Me_2Hg and elemental mercury. Differential pulse polarograms recorded after controlled potential reductive electrolysis of process II at a mercury pool electrode (potential held between processes II and III) shows the reappearance of process I for Me_2Hg and the maintenance of process III for MeHgCl. DC polarograms in the presence of Me_2Hg are similar in acetone to those reported in dichloromethane. However, in acetone, no wave attributable to formation of MeHgCl is observed after controlled potential electrolysis at a mercury pool electrode, and only process IIb is found when a voltammogram is recorded at a platinum electrode on the electrolysed solution. This suggests that process IIa corresponds to formation of a chloride-containing species.

All of the above data are consistent with the formation of two mercury rich alkyl mercury compounds, one of which contains chloride. In the absence of the chloride pathway the major oxidation process can be written in its simplest form as in eq 1. The simplest representation of

$$Me_2Hg + 2Hg \rightarrow Me_2Hg_3^{2+} + 2e^- \qquad (1)$$

this mercury-rich cation would be as the linear species. We have been unable to determine the exact nature of this species, and it could be either more highly polymerized or an alternative but closely related species. An equilibrium mixture of a range of species also cannot be ruled out nor can the involvement of coordinated perchlorate ligand. The reduction of the presumed $[Me_2Hg_3]^{2+}$ complex would then occur according to eq 2.

$$Me_2Hg_3^{2+} + 2e^- \rightarrow Me_2Hg + 2Hg \qquad (2)$$

In dichloromethane, but not in acetone, a second pathway is operative that is believed to involve reaction with chloride that either is present as an impurity or is extracted from the solvent.

In the absence of elemental mercury that is always present in a polarographic cell, mercuric chloride reacts directly with Me_2Hg to produce MeHgCl (eq 3),[1] and

$$Me_2Hg + HgCl_2 \rightarrow 2MeHgCl \qquad (3)$$

mercuric perchlorate reacts in an analogous way to form $MeHgClO_4$. Obviously, oxidation at mercury electrodes does not correspond to formation of mercury(II) perchlorate. As an alternative, mercury(I) generation could be involved so the chemistry of reaction of mercury(I) and Me_2Hg was investigated. Mercury(I) perchlorate is insoluble in dichloromethane. However, in acetonitrile or acetone the reaction of $Hg_2(ClO_4)_2$ with Me_2Hg proceeds smoothly. Figure 5 shows a polarogram recorded after the reaction of Me_2Hg with $Hg_2(ClO_4)_2$ in acetonitrile. Process IIb is observed as is the case after bulk electrolysis oxidation processes associated with Me_2Hg. Under DC polarographic conditions the pronounced maxima is observed, but the wave is no longer broad. At platinum electrodes, a single well-defined process IIb is observed. The chemical reaction is consistent with eq 4. Controlled potential

$$Me_2Hg + Hg_2(ClO_4)_2 \rightarrow [Me_2Hg_3](ClO_4)_2 \qquad (4)$$

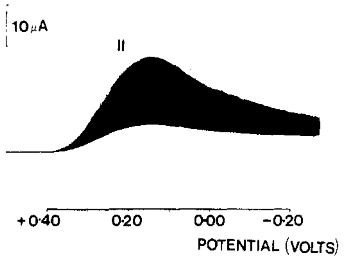

Figure 5. DC polarogram recorded after the reaction of $Hg_2(ClO_4)_2$ with Me_2Hg in acetonitrile (0.1 M Et_4NClO_4). Potentials recorded against an aqueous Ag/AgCl (3 M KCl) reference electrode. All other experimental parameters are as in Figure 1.

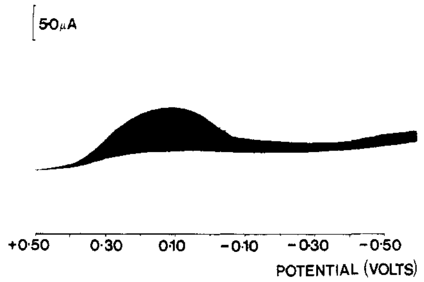

Figure 6. DC polarogram of a 5×10^{-4} M solution of MeHgCl in dichloromethane (0.1 M Bu_4NClO_4) recorded after the transfer of 0.5 coulomb during oxidative-controlled potential electrolysis at the potential of the mercury oxidation process (mercury pool electrode).

reductive electrolysis of the product formed this way produces the required concentration of Me_2Hg and elemental mercury at the ±8% confidence limit. Addition of Hg_2Cl_2 to $[Me_2Hg_3](ClO_4)_2$ leads to DC polarograms and platinum cyclic voltammograms similar to those observed after electrolysis of Me_2Hg at mercury electrodes in dichloromethane.

Reaction 5 is consistent with this observation, although again the exact formulation of the chloride-containing species could not be proved. The reduction process IIa

$$[Me_2Hg_3](ClO_4)_2 + Hg_2Cl_2 \rightarrow [Me_2Hg_5Cl_2](ClO_4)_2 \qquad (5)$$

observed at platinum electrodes after oxidative electrolysis of Me_2Hg at a mercury pool electrode is then defined as in eq 6.

$$[Me_2Hg_5Cl_2]^{2+} + 2e^- \rightarrow 2MeHgCl + 3Hg \qquad (6)$$

Further support for these reactions was obtained by conducting a controlled potential oxidative electrolysis experiment at a mercury pool electrode at a potential where mercury is oxidized (+0.85 V vs Ag/AgCl) in the presence of MeHgCl (Figure 6). Reduction process III for MeHgCl remains essentially unaltered during the course of the electrolysis. However a new reduction wave that has the potential and characteristics of process IIa grows in height. That is, the oxidation process at a mercury electrode in the presence of MeHgCl can be described by eq 7–10. These equations are the reverse of the equation

$$Hg \rightleftharpoons Hg^+ + e^- \qquad (7)$$

$$Hg \rightleftharpoons Hg^{2+} + 2e^- \qquad (8)$$

$$2MeHgCl + 2Hg^+ + Hg \rightarrow [Me_2Hg_5Cl_2]^{2+} \qquad (9)$$

$$2MeHgCl + Hg^{2+} + 2Hg \rightarrow [Me_2Hg_5Cl_2]^{2+} \qquad (10)$$

proposed for reduction process IIa and explain why the height of process III is unaltered during the reductive controlled potential electrolysis of process II that is now confirmed to be the summation of processes IIa and IIb

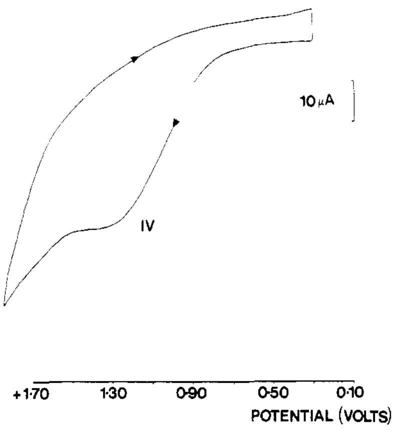

Figure 7. Cyclic voltammogram at a glassy carbon disk electrode (scan rate of 200 mV s^{-1}) for a 1.3×10^{-3} M solution of Me_2Hg in dichloromethane (0.1 M Bu_4NClO_4).

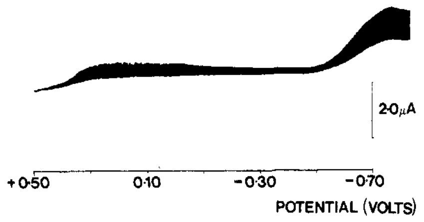

Figure 8. DC polarogram recorded after exhaustive oxidative electrolysis at a platinum gauze electrode for a 1.3×10^{-3} M solution of Me_2Hg in dichloromethane (0.1 M Bu_4NClO_4).

in dichloromethane. The source of the chloride in dichloromethane is unknown, but of course at positive potentials in the presence of chloride, mercury(I) and/or mercury(II) chloride will be formed at the electrode surface, so that the reactions described above can therefore take place. Gennett et al.[9] have recently noted that oxidation at mercury electrodes in dichloromethane in the presence of $M(CO)_2(\eta^5\text{-}C_5H_5)_2$ (M = Rh, Co) produces the mercuric chloride adduct $[Cl_2Hg]\cdot M(CO)_2(\eta^5\text{-}C_5H_5)_2$. Our work appears to resemble this study with respect to extraction of chloride from the solvent.

Undefined processes with characteristics similar to process(es) II were observed in polarograms recorded after the controlled potential electrolysis of tetraphenyllead under similar conditions to those described in this paper.[6] Diphenylmercury, which is known to be an initially formed product of electrolysis at a mercury pool electrode in the presence of tetraphenyllead, therefore is assumed to undergo analogous reaction pathways to dimethylmercury in bulk electrolysis experiments.

2. Oxidation of Me_2Hg at Platinum and Glassy Carbon Electrodes. Figure 7 shows a cyclic voltammogram for Me_2Hg recorded at a glassy carbon electrode in dichloromethane. The irreversible response at glassy carbon with a peak potential in the range 1.2–1.3 V vs Ag/AgCl (scan rate = 50–500 mV s^{-1}) and a similar response at platinum electrodes (not shown) occur at considerably more positive potentials than process I observed at mercury electrodes. The process at solid electrodes is therefore believed to be mechanistically different to process I at mercury electrodes and is labeled as process IV.

Controlled potential oxidative electrolysis at platinum gauze or glassy carbon electrodes produces the DC polarographic response shown in Figure 8. This process is similar to process II observed after electrolysis at mercury

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[9] Gennett, T.; Grzeszczyk, E.; Jefferson, A.; Sidur, K. M. *Inorg. Chem.* 1987, *26*, 1856.

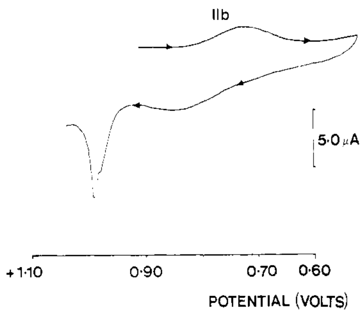

Figure 9. Cyclic voltammogram recorded at a platinum disk electrode (scan rate 200 mV s^{-1}) after exhaustive oxidative electrolysis at a platinum gauze electrode for a 1.3×10^{-3} M solution of Me_2Hg in dichloromethane (0.1 M Bu_4NClO_4).

pool electrodes with respect to the characteristic maxima but is less complicated. Significant concentrations of MeHgCl were detected as a product of electrolysis by the presence of a reduction process at the negative potentials where process III occurs. Cyclic voltammetry at a platinum electrode after oxidative electrolysis identifies a reduction response equatable to process IIb in the absence of process IIa (Figure 9). Reductive electrolysis of this solution at the platinum gauze electrode confirms that elemental mercury is produced as expected for process IIb. Polarographic analysis of the resultant solution of reductive electrolysis also confirms that Me_2Hg is a product of process IIb. Calculation of the number of moles of mercury deposited on the electrode (determined by the increased mass of the electrode) with respect to the number of moles of Me_2Hg recovered and the number of coulombs passed for exhaustive reductive electrolysis gives the simplest molecular formula for the species producing process IIb to be $Me_2Hg_3^{2+}$ at a confidence level of ±8%. The coulometric data for the oxidative electrolysis of process IV at solid electrodes is complicated by the high background currents at the potentials required for exhaustive electrolysis. However, all of the available data are consistent with eq 11 being the simplest representation of processes IV with $Me_2Hg_3^{2+}$ then being reduced according to eq 2.

$$3Me_2Hg \rightarrow Me_2Hg_3^{2+} + 4Me^{\bullet} + 2e^- \tag{11}$$

The first step at solid electrodes is believed to involve the simple electron-transfer process (12). The cation

$$Me_2Hg \rightarrow Me_2Hg^+ + e^- \tag{12}$$

radical Me_2Hg^+ has been reported to be formed by exposure of Me_2Hg to ^{60}Co γ-rays at 77 K in fluorotrichloromethane.[10] The present data indicate that this compound rapidly decomposes at ambient temperatures in dichloromethane. An equation consistent with the data is shown in eq 13. Presumably $Me^{\bullet}$ can dimerize or react with dichloromethane or adventitious water.

$$2Me_2Hg^+ + Me_2Hg \rightarrow Me_2Hg_3^{2+} + 4Me^{\bullet} \tag{13}$$

An important parallel to this work are studies of the electrochemical oxidation of mercury(II) diethyldithiocarbamate, $Hg(dtc)_2$.[11] The species $Hg_3(dtc)_4^{2+}$ was shown to exist in dichloromethane solution after oxidation in the presence of $Hg(dtc)_2$ at either platinum or mercury electrodes and evidence for other mercury-rich species was obtained. Removal of the solvent produced $Hg_5(dtc)_8^{2+}$, which has been characterized by an X-ray structural determination. Since MeHg(dtc) compounds are well-known,[12] the strong parallels in electrochemical behavior of Me_2Hg and $Hg(dtc)_2$ are not unexpected.

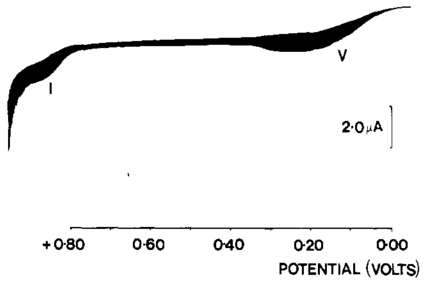

Figure 10. DC polarogram of a 1.75×10^{-4} M solution of Me_2Cd in dichloromethane (0.1 M Bu_4NClO_4). Other experimental parameters are as in Figure 1.

The polymeric mercury compound $Hg_5(dtc)_8Cl_2$ has been isolated from the reaction of Hg_2Cl_2 and sodium dithiocarbamate[13] and again parallels one of the species postulated as a minor product in this work. Compounds containing multiple mercury groups bonded to a single carbon atom (e.g. $C(HgOCOCH_3)_4$)[14] and many bimetallic species containing more than one mercury atom have been isolated. The cations, trimethyl(μ_3-selenoxo)trimercury ($[(MeHg)_3Se]^+$])[15] and (μ_4-arsenido)tetramethyltetramercury ($[(MeHg)_4As]^+$)[15] are two examples of charged bimetallic species. Polymeric mercury compounds, RHgHgR, adsorbed at mercury surfaces and in rapid equilibrium with R_2Hg in solution (eq 14) have also been well-documented.[16-18]

$$R_2Hg + Hg \rightleftharpoons RHgHgR(ads) \tag{14}$$

Di-*n*-hexyldimercury has also been reported as the product of reduction of 1,6-dibromohexane.[19a] This is an example of an isolated RHgHgR mercury(I) compound.

Reductive electrolysis of aryl- and alkylmercury chlorides in liquid ammonia[19b,c] produces a dark substance that has an electroconducting crystalline structure involving a polymeric arrangement of mercury and aryl (or aryl) ligands. Formation of cations of the kind $Me_2Hg_3^{2+}$ are therefore not totally unexpected. Unfortunately, attempts to isolate this species have been unsuccessful as on removing the solvent decomposition occurs to form other products.

3. Oxidation Processes in the Presence of Dimethylcadmium, Me_2Cd, at Mercury and Solid Electrodes. Figure 10 shows a DC polarogram in the presence of dimethylcadmium at a dropping mercury electrode in dichloromethane. Two oxidation processes with half-wave

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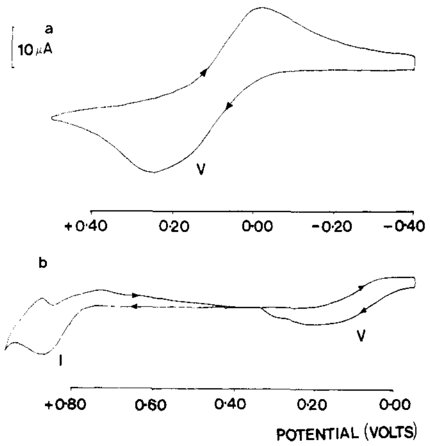

Figure 11. *Cyclic voltammograms obtained at a dropping mercury electrode for a* 6.9 × 10^{-4} M solution of Me_2Cd in dichloromethane (0.1 M Bu_4NClO_4). Scan rate: (a) 500 mV s^{-1} and (b) 100 mV s^{-1}. Other experimental parameters are as in Figure 2.

potentials of about 0.1 and 0.8 V vs Ag/AgCl are observed and are labeled processes V and I, respectively. Process V is complicated by a severe maximum at concentrations greater than 10^{-4} M. Plots of the limiting current at more positive potentials than the maximum against the square root of the mercury column height and against concentration show that the limiting current in dilute solutions is close to diffusion-controlled. Comparison of the DC polarographic wave height for process V to that obtained from an equimolar solution of tetramethyllead (which produces a known one-electron oxidation process at mercury[7] suggests that process V is a two-electron process. Comparison of process I to a DC polarogram for Me_2Hg (Figure 1) confirms that this compound is a product of process V. Since process I is a two-electron oxidation step and process V is of equal height, then process V is confirmed to also be a two-electron process that produces 1 mol of Me_2Hg/mol of Me_2Cd.

Cyclic voltammetry of process V at a growing mercury drop electrode indicates that at a scan rate of 100 mV s^{-1} that process V is irreversible whereas with a scan rate of 500 mV s^{-1} a significant degree of chemical reversibility is exhibited (Figure 11a). By extending the oxidative cyclic scan toward more positive potentials (Figure 11b), process I for Me_2Hg can be observed, as is the case under polarographic conditions.

As noted above, oxidation processes for Me_2Hg parallel processes described for mercury dithiocarbamates. For cadmium dithiocarbamates, the electrode process at mercury is reversible (eq 15).[20] An analogous process can

$$Cd(dtc)_2 + Hg \rightleftharpoons Hg(dtc)_2 + Cd^{2+} + 2e^- \qquad (15)$$

be proposed for Me_2Cd. Exchange reactions of diarylthallium cations at mercury surfaces involve $[Ar\text{–}Tl\text{–}Hg\text{–}Ar]^+$-type compounds,[21] and presumably analogous cadmium intermediates, Me–Cd–Hg–Me, are involved in the electrode process for Me_2Cd. Diarylthallium cations are isoelectronic with diarylcadmium. The irreversibility at slow scan rates is attributed to nucleation and precipitation of cadmium perchlorate. On the long time scale the overall reaction scheme may be written as in eq 16.

$$Me_2Cd + Hg \rightarrow Me_2Hg + Cd^{2+} + 2e^- \qquad (16)$$

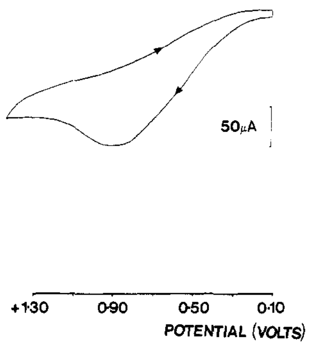

Figure 12. Cyclic voltammogram at a scan rate of 200 mV s^{-1} obtained at a glassy carbon disk electrode for a 1.4 × 10^{-3} M solution of Me_2Cd in dichloromethane (0.1 M Bu_4NClO_4).

The inherent instability of Me_2Cd makes quantitative coulometry with controlled potential electrolysis experiments difficult as this compound decomposes slowly during this long time scale experiment. Consequently, apparently low *n* values for electron transfer of 1.7 ± 0.3 are obtained at the mercury pool electrode when controlled potential electrolysis experiments are performed at +0.40 V vs Ag/AgCl. During the electrolysis a white precipitate is formed. This precipitate was shown to be cadmium perchlorate by dissolution in water and polarograhic examination. Electrolysis at potentials more positive than process II in the absence of light is exhausted after the transfer of 3.3 ± 0.2 electrons per molecule of Me_2Cd. A white precipitate of inorganic cadmium(II) perchlorate is again observed, and polarograms of the electrolysed solution are identical with those obtained after the electrolysis of Me_2Hg at a mercury pool electrode. Coulometric data *for process V are consistent with the transfer of* between 1.5 and 2.0 electrons per molecule. Values less than two electrons per molecule of Me_2Cd are attributed to decomposition of Me_2Cd during the course of the electrolysis.

Figure 12 shows a cyclic voltammogram recorded for oxidation of Me_2Cd at a scan rate of 200 mV s^{-1} at a glassy carbon electrode in dichloromethane. A similar response is found at a platinum electrode. A well-defined chemically irreversible oxidation process is observed at +0.9 V vs Ag/AgCl. The oxidation process occurs at a substantially more positive potential than oxidation processes at mercury electrodes. The voltammetric peak or limiting current height for the oxidation process at a glassy carbon electrode under stationary and rotating conditions is consistent with this being a two-electron process by comparison to related reference materials. Controlled potential electrolysis at a platinum gauze electrode produced insoluble cadmium perchlorate in contrast to the electrolysis of Me_2Hg where insoluble mercuric perchlorate is not seen. The oxidation process appears to be quite different to that of Me_2Hg and corresponds to eq 17. The results at mercury, platinum,

$$Me_2Cd \rightarrow Cd^{2+} + 2Me^{\bullet} + 2e^- \qquad (17)$$

and glassy carbon electrodes indicate that stable complexes of the kind $[Me_2Cd_3]^{2+}$ are not formed. Hg(I) is a stable oxidation state for mercury, whereas the corresponding Cd(I) species is virtually unknown. The role of Hg(I) intermediates are believed to be crucial in the formation of $[Me_2Hg_3]^{2+}$.

Registry No. Me_2Hg, 593-74-8; Me_2Cd, 506-82-1.

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