

Novel aspects of electrochemical oxidation of inorganic compounds in non-coordinating media

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Abstract - Distinct differences in chemical oxidation and electrochemical oxidation reaction pathways may lead to isolation of different products. Chemical oxidants commonly participate in oxidative addition reactions which increase the co-ordination number whereas in non-coordinating solvents highly activated co-ordinatively unsaturated species can be generated by oxidation at an electrode surface. However, with electrochemical oxidation, the role of the so-called inert electrolyte anion such as perchlorate, tetrafluoroborate or hexafluorophosphate may be crucial. Novel aspects of electrochemical oxidation are illustrated by (i) the oxidation of amalgam electrodes in dichloromethane and benzene to generate highly activated cations which then form perchlorate, or tetrafluoroborate complexes prior to precipitation of neutral metal salts and (ii) oxidation of six co-ordinate zero valent chromium, molybdenum and tungsten complexes at platinum electrodes in the same solvents to produce co-ordinatively unsaturated oxidation state one and two species which are prone to nucleophilic attack by the perchlorate electrolyte. In contrast to differences observed in oxidation studies, chemical and electrochemical reduction pathways are likely to produce the same products because reductive elimination reactions can occur in both cases.

INTRODUCTION

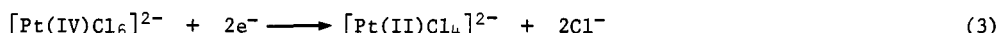
Redox processes constitute an important class of inorganic chemical reaction and may be studied by chemical, electrochemical and other methods. Chemical oxidants often play a specific role in the overall process and therefore may lead to different reaction pathways to those observed with electrochemical oxidation. For example, oxidative addition reactions such as



are very common. In this class of reaction, both the oxidation state and the co-ordination number of the metal increase after oxidation. Electrochemical oxidation reactions may differ from chemical oxidation, in that co-ordinating ligands are not usually available. Thus, highly reactive, co-ordinatively unsaturated compounds, designated as $[\text{B}]^{n+}$ in equation 2, are likely to be generated after an electron transfer process involving oxidation of compound A in an inert medium (non co-ordinating solvent and electrolyte).



In contrast, electrochemical reduction processes such as



and chemical reduction processes are very likely to follow analogous reduction pathways (reductive elimination) since elimination of a ligand can take place in either case.

In this paper, examples of electrochemical oxidation processes of inorganic compounds will be given to emphasise the novel aspects arising from the use of this method of oxidation as an alternative to chemical oxidation. In particular, the role of the electrolyte and solvent will be reviewed when highly reactive and co-ordinatively unsaturated compounds are generated at an electrode surface. The examples used to illustrate the principles of electrochemical oxidation in non-coordinating media are the oxidation of metallic electrodes to their metal cations (non-solvated (?)) and oxidation of zero valent six-coordinate metal carbonyl complexes. The principles are believed to be valid to many areas of oxidative redox chemistry.

ELECTROCHEMICAL GENERATION OF SOLUBLE AND REACTIVE METAL CATIONS IN DICHLOROMETHANE AND BENZENE

Spectroscopic methods have demonstrated that metal ions exist in aqueous media as strongly co-ordinated species of the kind $[\text{M}(\text{H}_2\text{O})_x]^{n+}$. In co-ordinating organic solvents, analogous

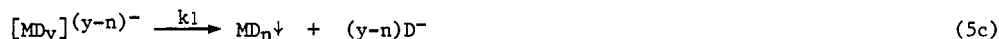
complexes of the type $[MS_x]^{n+}$ ($S = \text{solvent}$) have been observed, with the anions necessarily present in these studies to balance the charges being assumed to be non-coordinating. Initially, nitrate was used as a non-complexing anion, but this has now been shown to be a co-ordinating ligand with many metals. Recent studies have focussed on anions such as $[\text{ClO}_4]^-$, $[\text{BF}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$ and $[\text{PF}_6]^-$, which generally have been verified to be non-coordinating, except in special situations.

Solvated forms of metal ions, $[MS_x]^{n+}$, cannot be expected to be as reactive as the non-coordinated cation, M^{n+} , since the free energy of the metal ion has been lowered by the reaction given in equation 4. The energies of formation of $[M(S)_x]^{n+}$ are described



by the classic Born-Haber cycle. In principle, non-coordinating solvents should enable studies to be undertaken on non-solvated M^{n+} metal cations by dissolution of appropriate metal salts. However, in the vast majority of cases, metal salts containing non-coordinating anions are insoluble in such solvents, which commonly have low dielectric constants. Consequently, virtually no solution data on soluble forms of simple metal salts are available in non-coordinating media, e.g. hydrocarbons, aromatic hydrocarbons, and halogenated hydrocarbons.

Recent work from these laboratories has demonstrated the possibility of electrochemically generating M^{n+} cations in solvents such as dichloromethane and benzene [1]. Electrochemical oxidation of a metal electrode in the presence of non-coordinating solvent and electrolyte, $[C^+][D^-]$, is expected to occur by reactions 5a to 5c



If equations 5a and 5b occur at a diffusion-controlled rate, and the rate constant for precipitation, k_1 , is sufficiently slow so that reaction 5c is unimportant on the electrochemical time scale, electrochemical measurements may provide thermodynamic data on the soluble species M^{n+} and $[MD_y]^{(y-n)-}$. That is, even if $[D]^-$ is classically regarded as a non-coordinating ligand that usually participates only in ion-pair formation, under the special conditions described above, it is predicted that an unusually ligated metal ion will be formed.

Thermodynamic descriptions of electrochemical oxidation of a pure metal electrode are often complicated by surface phenomena. However, it has been demonstrated that oxidations of certain metal amalgam electrodes are usually well-defined. In particular, theoretical descriptions for the dropping amalgam electrode are available [2].

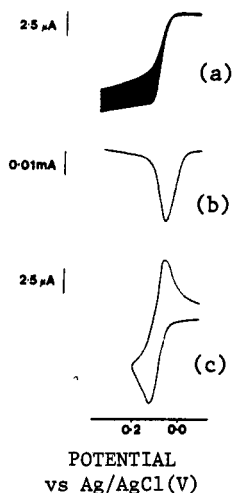
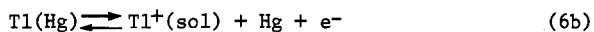
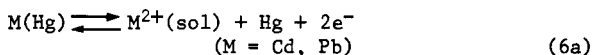


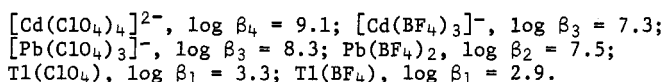
Figure 1. Voltammetric curves for the oxidation of a lead amalgam electrode in dichloromethane containing 0.2 M $[\text{NBu}_4][\text{ClO}_4]$: (a) dc polarogram, (b) differential-pulse polarogram, (c) cyclic voltammogram. Further details available in [1].

Figure 1 shows typical oxidative DC polarograms, differential-pulse polarograms, and cyclic voltammograms obtained at a dropping Pb amalgam electrode in a solution of dichloromethane containing 0.2 M $[\text{NBu}_4][\text{ClO}_4]$ as the supporting electrolyte. For dilute amalgams, plots of E versus $\log(i/(i-i_d))$ are close to the theoretically expected values [29 mV (Cd,Pb) and 58 mV (Tl)] for formation of a soluble product in dichloromethane at 20°C. That is, the reactions are as shown in equations 6a and 6b.



If an insoluble product such as $\text{Cd}(\text{ClO}_4)_2$, $\text{Pb}(\text{ClO}_4)_2$, or TlClO_4 had resulted, then a different response would have been predicted theoretically. It is possible that nucleation and precipitation reactions cause the erratic behaviour observed at high amalgam concentrations, but importantly the kinetics of precipitation must be sufficiently slow so as not to influence the result under conditions where the amalgam is dilute.

Oxidation at Cd, Pb, and Tl dropping amalgam electrodes in a solution containing dichloromethane and either $[\text{NBu}_4][\text{PF}_6]$ or $[\text{NBu}_4][\text{BF}_4]$, also occur reversibly. The $[\text{PF}_6]^-$ ligation is considerably weaker than that of $[\text{ClO}_4]^-$ or $[\text{BF}_4]^-$. Data obtained in dichloromethane with hexafluorophosphate as a reference electrolyte [1] allowed the following complexes with their equilibrium constants to be identified:



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 co-ordinating solvents such as dimethyl sulfoxide, acetonitrile etc. are added to dichloromethane (0.2 M $[\text{NBu}_4][\text{PF}_6]$) solutions [3].

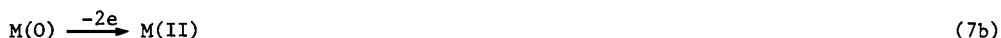
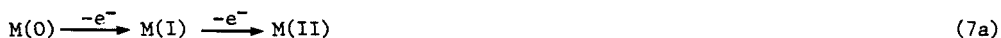
Controlled potential electrolysis experiments at an amalgam pool electrode in dichloromethane lead to the formation of the expected non-solvated insoluble salts, demonstrating that the kinetics of precipitation are slower than the polarographic time scale. Concepts developed in this work on electrochemical oxidation in inert media provide prospects for new forms of methanistic, thermodynamic and synthetic metal ion chemistry [1,3].

ELECTROCHEMICAL OXIDATION OF ZERO VALENT CHROMIUM, MOLYBDENUM AND TUNGSTEN CARBONYL COMPLEXES

Chromium, molybdenum and tungsten form an extremely large variety of highly stable, zero valent six co-ordinate complexes (e.g. $\text{M}(\text{CO})_6$, $[\text{M}(\text{CO})_5\text{Cl}]^{-}$, $\text{M}(\text{CO})_4(\text{PPh}_3)_2$; M = Cr, Mo, W). These zero valent complexes have an eighteen electron configuration and are said to obey the effective atomic number rule [4].

Chemical oxidation of these zero valent molybdenum and tungsten complexes with halogens, frequently leads to the formation of stable seven co-ordinate oxidation state two complexes (e.g. $[\text{Mo}(\text{CO})_4\text{I}_3]^{-}$) via oxidative addition reactions [4,5]. In view of the increase in coordination number accompanying chemical oxidation, these seven co-ordinate oxidation state two complexes retain the stable eighteen electron configuration of their zero valent counterparts, although six co-ordinate seventeen electron oxidation state one and six co-ordinate sixteen electron oxidation state two complexes are sometimes reported to be the product of chemical oxidation of zero valent molybdenum and tungsten carbonyl complexes [5]. Chemical oxidation of chromium carbonyl complexes generally produces non-carbonyl containing chromium(II), or chromium(III) complexes, with seventeen electron six co-ordinate oxidation state one complexes being observed on some occasions and eighteen electron seven co-ordinate complexes on relatively rare occasions. Differences observed between chromium and the other two elements are usually attributed to the smaller size of the first row transition metal, which makes the formation of stable seven co-ordinate complexes less likely than with the relatively large molybdenum and tungsten metals.

Electrochemical oxidation of zero valent complexes in non co-ordinating media usually occurs via two discrete one electron steps (equation 7a) or by a single two electron process (equation 7b).



In electrochemical experiments in dichloromethane [6,7] oxidation of $[\text{Cr}(\text{CO})_5\text{X}]^{-}$ (X = F, Cl, Br, I) shows evidence of six co-ordinate $\text{Cr}(\text{CO})_5\text{X}$ and $[\text{Cr}(\text{CO})_5\text{X}]^{+}$, but the sixteen electron species, typical of almost all chromium carbonyl electrochemical oxidation studies, leads to a non carbonyl containing product on the synthetic time scale associated with bulk controlled potential oxidative electrolysis. That is,



In dichloromethane or benzene, electrochemical oxidation of $\text{Cr}(\text{CO})_3(\text{arene})$ [8,9] leads to the observation of a single two electron oxidation process with ClO_4^{-} as the electrolyte anion to produce Cr^{2+} , arene and carbon monoxide, but occurs via two single electron

processes and a stable $[\text{Cr}(\text{CO})_3(\text{arene})]^+$ intermediate if PF_6^- is the anion (Figure 2). That is, ClO_4^- acts as a ligand (nucleophile). In the case of a complex containing pendant phosphines (Figure 3), electrochemical oxidative addition to six co-ordinate $\text{M}(\text{CO})_3(\eta^2\text{-P-P})(\eta^1\text{-P-P})$ (P-P = potentially bidentate phosphine such as 1,2-bis(diphenylphosphine)ethane) can occur to produce moderately stable $[\text{M}(\text{CO})_3(\eta^2\text{-P-P})]^{2+}$ seven coordinate dipositive complexes (M = Mo, W) which have not been synthesised chemically. This is a special class of oxidative addition achieved under electrochemical conditions [10].

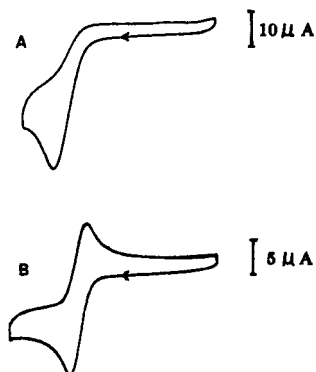


Figure 2. Cyclic voltammograms for oxidation of 5×10^{-4} M $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in dichloromethane at a glassy carbon electrode (scan rate = 200 mV s^{-1}) (A) ClO_4^- electrolyte; (B) PF_6^- electrolyte. Further details available in reference 6.

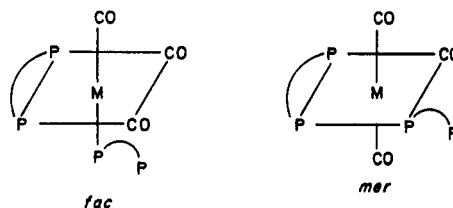


Figure 3. Structural representation of six co-ordinate fac- and mer- $\text{M}(\text{CO})_3(\eta^2\text{-P-P})(\eta^1\text{-P-P})$ compounds.

If the electrolyte can be eliminated or is an exceptionally poor ligand such as hexafluorophosphate, then the six co-ordinate seventeen electron and sixteen electron carbonyl containing species are always likely to be accessible by electrochemical oxidation in a non-coordinating solvent. In contrast, relatively rarely will the chemical oxidant be an innocent participator in the oxidation process and a seven co-ordinate eighteen electron carbonyl containing complex or a non-carbonyl containing species is likely to be produced.

Acknowledgements

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