

Communications

Cyclic Voltammetric Study of Electron Transfer Equilibria Involving Iron(II, III) & Protons

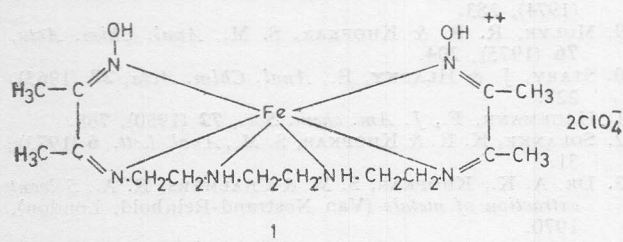
J. G. MOHANTY & A. CHAKRAVORTY

Department of Chemistry, Indian Institute of Technology
Kanpur 208016

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The cyclic voltammetric response of an iron(II) species derived from a hexadentate ligand containing two dissociable protons is investigated as a function of pH . The equilibrium redox reaction involves an integral reversible step in which two protons and one electron participate. The formal oxidation potential of the couple is found to be 0.65 ± 0.01 V (vs SCE).

CYCLIC voltammetry is a powerful technique for studying a full cycle of oxidation and reduction starting either from the reductant or oxidant¹. A versatile instrument² built in this laboratory uses platinum as the working electrode and has a wide scan-rate capability. We wish to report here interesting pH -dependent cyclic voltammetric response (25°C) obtained by using the purple salt, $Fe(H_2L)(ClO_4)_2$ having low-spin pseudooctahedral iron(II) in a FeN_6 core³ (H_2L is the hexadentate ligand in 1; the oxime protons are dissociable) as shown in 1.



The pH of the medium was controlled using $CH_3COONa-HCl$ in 0.1M NaCl. The buffer also acted as the supporting electrolyte. The solute concentration was $\sim 10^{-3}M$. All potentials were measured with reference to saturated calomel electrode (SCE).

It is known³ that appreciable proton dissociation from $Fe(H_2L)^{2+}$ occurs only above pH 4 yielding $Fe(HL)^+$ and finally FeL . The present measurements were done below pH 4 so that the starting species was solely $Fe(H_2L)^{2+}$. Representative results are shown in Table 1 and Fig. 1. Let E_{pa} and E_{pc} be the anodic and cathodic peak potentials and ΔE_p be the separation between them. The observed values of ΔE_p lies in the range 60-70 mV. This clearly shows⁴ that reversible one electron electrode process is involved. Controlled potential oxidation of $Fe(H_2L)^{2+}$ at $E > E_{pa}$ fully corroborates the one-electron involvement. Although ΔE_p does

TABLE 1 — CYCLIC VOLTAMMETRIC DATA^{a,b} (298°K)

pH	ΔE_p	$0.5(E_{pa} + E_{pc})$	$0.118 pH$	E_{298}°
1.55	0.065	0.463	0.18	0.64
1.85	0.060	0.430	0.22	0.65
2.65	0.070	0.340	0.31	0.65
3.50	0.070	0.245	0.41	0.66

(a) All potentials are in volt with reference to SCE.
(b) ΔE_p , E_{pa} and E_{pc} are independent of scan rate in the range 0.01-0.20 V sec⁻¹.

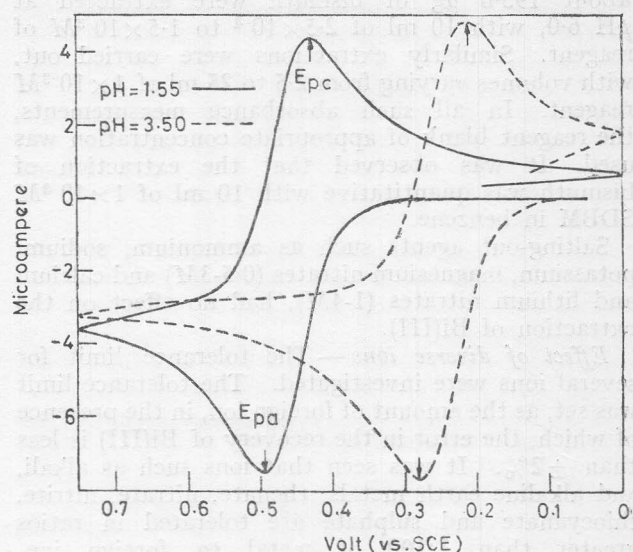
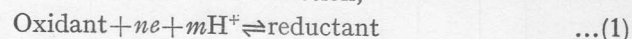


Fig. 1 — Cyclic voltammogram of $Fe(H_2L)(ClO_4)_2$ at two pH values

not change, E_{pa} and E_{pc} vary sensitively with pH . Clearly protons are involved in the electrode reaction.

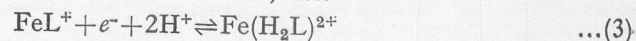
For the electrode reaction,



the formal electrode potential, E_{298}° can be shown^{2,4} to be given by

$$E_{298}^{\circ} = 0.5(E_{pa} + E_{pc}) + 0.059(m/n)pH \quad \dots(2)$$

The observed experimental results are in excellent agreement with the electrode reaction in which $m = 2$ and $n = 1$, i.e.



For reaction (3) we have from Eq. (2),

$$E_{298}^{\circ} = 0.5(E_{pa} + E_{pc}) + 0.118pH \quad \dots(4)$$

Using Eq. (4) and experimental data, E_{298}° is found to be (Table 1) 0.65 ± 0.01 (vs SCE). In solution the iron(III) species FeL^+ is yellow in colour. Attempts are being made to isolate it as salts. Further cyclic voltammetric investigations on the redox properties of this and other related systems containing iron is in progress.

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References

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On the Nature of Diphenylselenium Dichloride

R. C. PAUL & KULDIP K. BHASIN

Department of Chemistry, Panjab University
Chandigarh 160014

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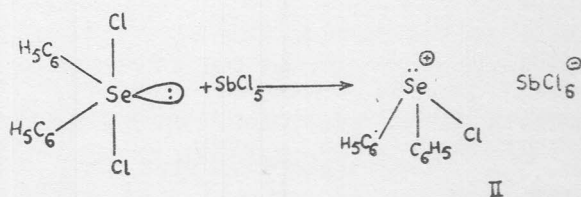
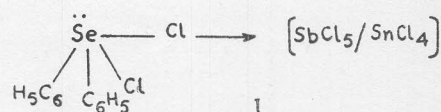
Stabilization and characterization of monochloro-diphenylselenium ion, $(C_6H_5)_2SeCl^+$, in the form of its adducts with $SbCl_5$ and $SnCl_4$ is being reported for the first time. The adducts are assigned ionic structures on the basis of IR and conductance data.

PEACH¹ while titrating diphenylselenium dichloride against boron trichloride in liquid hydrogen chloride, suggested the possible formation of $(C_6H_5)_2SeCl^+BCl_4^-$ which decomposed immediately after the removal of the solvent. Similar observation was made by Wynne and Pearson² who found that boron trifluoride causes the decomposition of diphenylselenium difluoride. They attributed the decomposition to the formation of $(C_6H_5)_2SeX^+$, an electrophile, which attacks the phenyl groups of diphenylselenium dihalide leading to the formation of a polymer. In this communication we report for the first time the stabilization and characterization of $(C_6H_5)_2SeCl^+$ ion by forming its stable adducts with antimony pentachloride and tin tetrachloride.

The adducts were prepared by mixing $SbCl_5$ and $SnCl_4$ in 1:1 and 1:2 molar ratio respectively with the ice-cold solutions of diphenylselenium dichloride in a small quantity of thionyl chloride. Addition of carbon tetrachloride to the reaction mixture resulted in the precipitation of a moisture-sensitive yellow crystalline compound in the case of antimony pentachloride and a white compound in the case of tin tetrachloride. The complexes were washed with carbon tetrachloride and dried *in vacuo*. $(C_6H_5)_2SeCl_2 \cdot SbCl_5$ [Found: Se, 12.93; Cl, 40.32; Sb, 19.70. Required: Se, 13.12; Cl, 41.21; Sb, 20.10%]; m.p., 74-76°. $2(C_6H_5)_2SeCl_2 \cdot SnCl_4$ [Found: Se, 17.65; Cl, 30.84; Sn, 12.92. Required: Se, 18.23; Cl, 31.57; Sn, 13.66%]; m.p. 80-81°. Molecular weights of the adducts could not be determined due to extensive dissociation.

The characteristic IR absorption bands associated with Sn-Cl, Sb-Cl and Se-Cl groups have been used

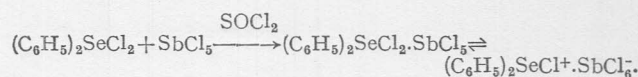
to characterize the adducts. IR bands associated with the benzene nucleus in the adducts are out being reported as they virtually remain unchanged on complex formation³. The $\nu(Se-C)$ bands in pure diphenylselenium dichloride⁴ appear at 466 and 478 cm^{-1} whereas in the adducts these are shifted to lower frequencies, viz. 447, 463 cm^{-1} and 452, 465 cm^{-1} in the adducts of antimony pentachloride and tin tetrachloride respectively. Wynne and George⁴ have assigned the absorption band appearing at 310 cm^{-1} in diphenylselenium dichloride to $(Se-Cl)$ stretching frequency. While no band is present around 310 cm^{-1} in the spectra of the adducts, new bands appearing at 380 cm^{-1} ($SbCl_5$ adduct) and 370 cm^{-1} ($SnCl_4$ adduct) can be assigned to $\nu(Se-Cl)$. The positive shift in $\nu(Se-Cl)$ would not be expected if the adducts were halogen-bridged (I).



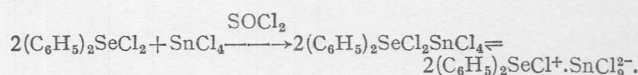
However, this positive shift can be understood in the light of the formation of an ionic structure of the type (II) in which one halogen changes place from an apical to a pyramidal⁵ one in the overall trigonal-bipyramidal structure.

The presence of a new strong-intensity band at 330 cm^{-1} in the case of antimony pentachloride adduct and bands at 305 and 272 cm^{-1} in the case of tin tetrachloride adduct are in agreement with the above structure as these are the regions where the characteristic absorption bands arising from $[SbCl_6]^-$ and $[SnCl_6]^{2-}$ species occur^{6,7}. The molar conductance values of the adducts of antimony pentachloride and tin tetrachloride in dichloromethane (13.34 and 28.48 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) further support⁸ the ionic nature of the adducts.

Therefore, the adduct formation may be represented as:



and



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