

Spectroelectrochemical Investigation of Pentacarbonyl(pyrazine)metal(0) (Metal = Cr, Mo, W) Complexes of Group 6 Elements

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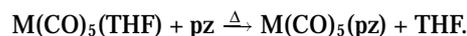
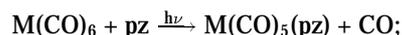
Pyrazine, Metal Carbonyls, Cyclic Voltammetry

The electrochemical behaviour of pentacarbonyl(pyrazine)metal(0) complexes of the group 6 elements was studied by cyclic voltammetry in dichloromethane-(*n*-Bu)₄NBF₄ solvent-electrolyte couple at –20 °C vs. Ag/Ag⁺ or SCE reference electrode. Constant potential electrolyses of the complexes were carried out at their first oxidation peak potentials and monitored in situ by UV-Vis spectrometry. Electrolysis of W(CO)₅pz produces [W(CO)₅pz]⁺ and a similar electrochemical mechanism is expected both for Cr(CO)₅pz and Mo(CO)₅pz complexes. In situ low temperature constant current ESR electrolysis also confirmed the production of [W(CO)₅pz]⁺ after the electron transfer.

Introduction

Transition metal carbonyl complexes are the basic starting materials for the synthesis of many organometallic compounds, which are mainly used as catalysts for the reactions of unsaturated hydrocarbons [1 - 6]. Various types of carbonyl-donor ligand metal complexes have been prepared via ligand substitution reactions. Especially, photo substitution of group 6 metal carbonyl complexes has been established with high quantum yields and has found wide range of applications, mainly with π -donor ligands (diolefine, diimine, dialkylphosphinoalkane) [7 - 9]. Among these potential ligands, pyrazine is one of the most interesting. It is an excellent π acceptor ligand because of its relatively low energy π^* orbitals, which facilitate electron transfer between metal and pyrazine [10 - 11]. Pyrazine and substituted pyrazines have long been known to form linear bridges between the metal ions generating oligomeric species [12 - 15] or polymeric arrays [16, 17] in the presence of metals atoms containing more than one oxidation state. Beside this, Creutz-Taube type of complexes have been prepared [18], in which pyrazine acts as a bridging ligand between two pentaammine ruthenium units. Pyrazine containing group 6 metal carbonyl complexes have also been known and can be prepared either by direct photolysis of M(CO)₆ (M = Cr, Mo W) with

pyrazine (pz), or M(CO)₅(THF) (M = Cr, Mo, W) complexes can react thermally with the pyrazine ligand according to the reactions



Pyrazine bridged homobimetallic and heterobimetallic complexes have been prepared from M(CO)₅(pz) or M(CO)₅(THF) (M = Cr, Mo W). Zulu et al. [12] have reported on the photophysical, photochemical and redox behaviour of such complexes. However, no details of electrochemical oxidation and reduction of these complexes were mentioned. In order to get more information on the redox behaviour of pentacarbonyl(pyrazine)metal(0) (metal = Cr, Mo, W) complexes, we have investigated the electrochemical oxidation of the complexes via in situ UV-Vis spectroscopic techniques. Furthermore, the origin of the electron transfer, whether it is metal centered or not, have been investigated via in situ ESR studies.

Experimental

Preparation of the compounds

All reactions dealing with the preparation of the complexes were carried out either in vacuum or under dry and deoxygenated nitrogen atmosphere. Solvents were

distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen atmosphere for 3 - 4 days. Hexacarbonylmetal(0) and pyrazine were purchased from Aldrich Chemical Co. Ltd, Dorset, England and used as received. NMR spectra were recorded on a Bruker DPX 400 Spectrometer. Infrared spectra were recorded from 1,2-dichloroethane solutions using Perkin Elmer PC-16 FTIR or Nicolet 510 FTIR spectrometers. Mass spectra were taken from a MAT 8200 instrument using Electron Impact Ionization methods.

Pentacarbonyl(pyrazine)chromium, Cr(CO)₅(pz): The synthesis of Cr(CO)₅(pz) (pz = pyrazine) was carried out by the thermal reaction of 0.576 mmol of Cr(CO)₅(ZCO) (ZCO = cis-cyclooctene) [19] with 0.864 mmol of pyrazine in deoxygenated n-hexane under argon atmosphere. After the completion of the thermal reaction, n-hexane was removed under high vacuum. The purification was achieved by column chromatography on silica. Pyrazine was eluted by n-hexane, while for the product 50% hexane-dichloromethane mixture was used as eluent. Recrystallization from dichloromethane solution yielded reddish crystals (80% yield). - IR (dichloromethane): $\nu(\text{C}=\text{O})$ 2067, 1947, 1920 cm^{-1} . - ¹³C-{1H-NMR} (100.613 MHz, CD₂Cl₂): δ = (150.30 (M-N=C), 146.10 (N=C), 220.70 (C=O), 214.18 (C=O)). - ¹H-NMR (400.132 MHz, CD₂Cl₂): 8.62 (M-N-CH), 8.45 (N-CH).

Pentacarbonyl(pyrazine)molybdenum, Mo(CO)₅(pz), and pentacarbonyl(pyrazine)tungsten, W(CO)₅(pz): M(CO)₅(pz) (M = Mo, W) were prepared by the thermal reaction of M(CO)₅(THF) with pyrazine as described in the literature [20]. THF was removed completely and the product was washed several times with n-hexane to remove the unreacted M(CO)₆. (Yield = 85% for Mo(CO)₅(pz); 93% for W(CO)₅(pz)). - IR (dichloromethane): For Mo(CO)₅(pz): $\nu(\text{C}=\text{O})$ 2072, 1949, 1914 cm^{-1} . - ¹³C-{1H-NMR} (100.613 MHz, CD₂Cl₂): δ = (148.24 (M-N=C), 145.63 (N=C), 203.21 (C=O), 200.48 (C=O)). - ¹H-NMR (400.132 MHz, CD₂Cl₂): 8.57 (M-N-CH), 8.52 (N-CH). For W(CO)₅(pz): $\nu(\text{C}=\text{O})$ 2069, 1942, 1912 cm^{-1} . - ¹³C-{1H-NMR} (100.613 MHz, C₂D₆CO): δ = (151.40 (M-N=C), 148.30 (N=C), 202.99 (C=O), 199.17 (C=O)). - ¹H-NMR (400.132 MHz, C₂D₆CO): 9.07 (M-N-CH), 8.74 (N-CH). Molecular peak (m/z = 404).

Electrochemistry

Cyclic voltammograms of the complexes were recorded by using a Potentiostat Wenking POS 73 Potentiostat with a Llyod PL3 XY/t recorder. Cyclic voltammetry studies were carried out in dichloromethane solution containing 0.1 M [(n-C₄H₉)₄N]BF₄ as the supporting electrolyte. Redox potentials of the complexes

Table 1. Cyclic voltammetry data for M(CO)₅pz [M = Cr(0), Mo(0), W(0); pz = pyrazine], at platinum electrode in dichloromethane at -20 °C. VSR = 200 mV/s.

Compound	E _a (V)	E _c (V)	RE
Cr(CO) ₅ pz	1.10(rev) (I _a)	-0.30 • (I _c)	SCE
	1.50 (II _a)	-0.90 • (II _c)	
	0.80 (rev) (I _a)	-0.50 (I _c)	Ag/Ag ⁺
	1.20 (II _a)	-1.10 (II _c)	
Mo(CO) ₅ pz	1.30 (I _a)	+0.30 • (I _c)	SCE
		-0.50 (II _c)	
		-0.90 (III _c)	
		-1.40 (IV _c)	
	1.05 (I _a)	+0.10 • (I _c)	Ag/Ag ⁺
W(CO) ₅ pz		-0.50 (II _c)	
		-0.85 (III _c)	
		-1.25 (IV _c)	
	1.30 (I _a)	0.75 ♦ (I _c)	SCE
	1.60 (II _a)	-0.15 ♦ (II _c)	
Pyrazine		-1.50 (III _c)	
	1.03 (I _a)	-1.50 (I _c)	Ag/Ag ⁺
	1.35 (II _a)	-1.95 (II _c)	
	2.10 (I _a)	0.30 ♦ (I _c)	Ag/Ag ⁺
		-0.25 ♦ (II _c)	

E_a represents oxidation peak potentials and E_c represents reduction peak potentials. ♦ Shows the dependence on the first oxidation peak and • shows the dependence on the last oxidation peak where RE represents the reference electrode, respectively.

were measured at a Pt-bead working electrode versus saturated calomel electrode (SCE) and Ag/AgBF₄ (0.1 M in CH₃CN or CH₂Cl₂) reference electrode, where a Pt-wire was used as an auxiliary electrode. Nitrogen gas was purged through the solution before taking the cyclic voltammograms to eliminate oxygen from the system. All of the studies were carried out at 200 mV/s. Concentration of the complex was about 0.001 M for each measurement.

Controlled potential coulometry experiments were performed by using a home made digital counter.

In situ controlled potential electrolysis at the first anodic peak potentials of the complexes were carried out in spectroscopic grade dichloromethane by using the same supporting electrolyte at -20 °C. The changes in the electronic absorption spectra of the complexes were followed by a HP 82524A Diode Array Spectrophotometer during the electrolysis. Spectra were recorded every 5 mC. 0.75 cm² platinum mesh working and auxiliary electrodes were used vs Ag/Ag⁺ reference electrode.

Electron spin resonance spectrometry

The ESR spectrum of the species generated during the constant current electrolysis were recorded by using a Varian E12 Spectrometer. Cell used for in situ ESR studies was described elsewhere [21].

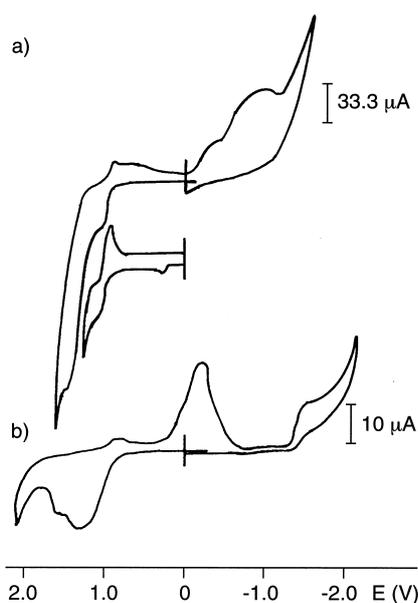


Fig. 1. Cyclic voltammograms of $\sim 10^{-3}$ M solution of a) $\text{Cr}(\text{CO})_5\text{pz}$ b) $\text{W}(\text{CO})_5\text{pz}$ in dichloromethane at -20°C , versus SCE. VSR: 200 mV/s.

Result and Discussion

Electrochemical behaviour

The electrochemical behaviour of $\text{M}(\text{CO})_5\text{pz}$ [$\text{M} = \text{Cr}, \text{Mo}$ and W ; $\text{pz} = \text{pyrazine}$] complexes has been studied in dichloromethane- $[(n\text{-C}_4\text{H}_9)_4\text{BF}_4]$ solvent-electrolyte couple under nitrogen atmosphere. Cyclic voltammetry studies were carried out at low temperature (i. e. -20°C), since the complexes, especially $\text{Cr}(\text{CO})_5\text{pz}$ and $\text{Mo}(\text{CO})_5\text{pz}$, decompose thermally in solution. The data are presented in Table 1. The cyclic voltammogram of $\text{Cr}(\text{CO})_5\text{pz}$ is given in Fig 1a. In the first anodic scan, two oxidation peaks at 1.10 V (rev) and 1.50 V vs. SCE were obtained. Upon reversal of the scan direction, two irreversible reduction peaks, that were dependent on the second oxidation peak, were observed at -0.30 and -0.90 V vs. SCE. The first oxidation peak (at 1.10 V) was found to be pseudo reversible.

In the case of $\text{Mo}(\text{CO})_5\text{pz}$, the cyclic voltammogram involves an irreversible oxidation peak at 1.30 V vs SCE in the first anodic scan. As the scan direction is reversed, four irreversible reduction peaks at 0.30, -0.50 , -0.90 and -1.40 V vs. SCE have been obtained.

The cyclic voltammogram of $\text{W}(\text{CO})_5\text{pz}$ (Fig. 1b) consists of two irreversible oxidation peaks and

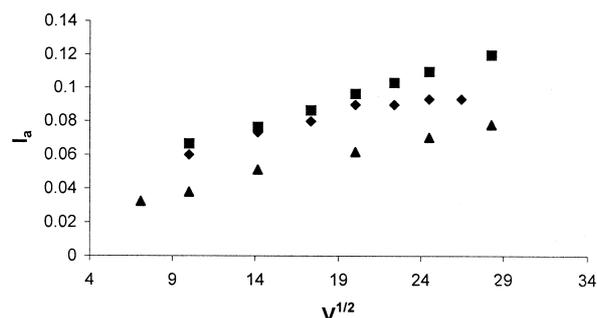


Fig. 2. Variation of the anodic current with the square root of voltage scan rate. \blacklozenge : $\text{Cr}(\text{CO})_5\text{pz}$, \blacksquare : $\text{Mo}(\text{CO})_5\text{pz}$, \blacktriangle : $\text{Cr}(\text{CO})_5\text{pz}$.

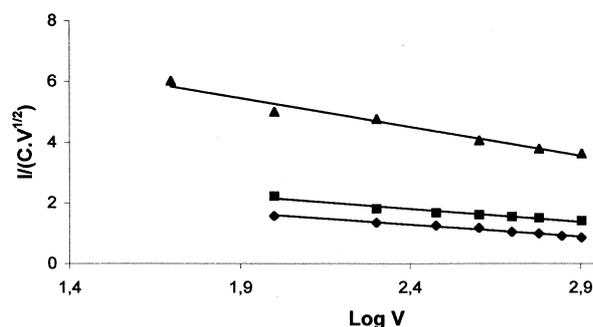


Fig. 3. Variation of current function $I/(C \cdot V^{1/2})$, with the logarithm of the voltage scan rate for the first oxidation peaks where I (mA) is the peak current, V (mV/s) the voltage scan rate and C (mol/L) the molar concentration. \blacklozenge : $\text{Cr}(\text{CO})_5\text{pz}$, \blacksquare : $\text{Mo}(\text{CO})_5\text{pz}$, \blacktriangle : $\text{Cr}(\text{CO})_5\text{pz}$.

three irreversible reduction peaks at 1.30, 1.60, 0.75, -0.15 and -1.50 V vs. SCE reference electrode, respectively. The first two reduction peaks, at 0.75 and -0.15 V, were dependent on the first oxidation peak at 1.30 V vs. SCE.

A brief inspection of the data given in Table 1 shows that the first oxidation potentials of the three complexes slightly increase going down the group, which is attributed to an increase in the metal-ligand π -interaction upon descending from chromium to tungsten [22].

A plot of the peak current (I_a) versus the square root of voltage scan rate ($V^{1/2}$) is given in Fig. 2. A linear relationship was observed between them in the range of scan rates from 50 to 1000 mV/s (Fig. 2). The positive slope in Fig. 2 indicates a diffusion controlled electron exchange reaction at I_a for all three complexes. The plot of current function ($I/(C \cdot V^{1/2})$), where I is the peak current, V is the voltage scan rate, and C is the molar concentration,

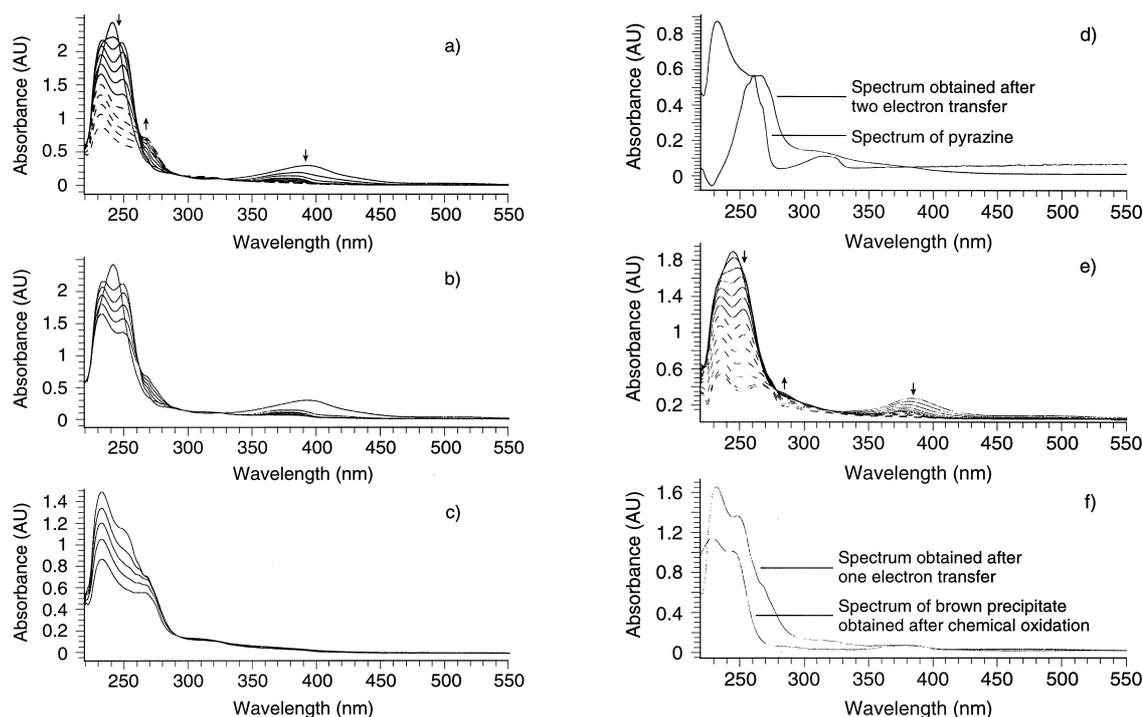


Fig. 4. The changes in the electronic absorption spectrum of 6.20×10^{-5} M $W(CO)_5pz$ in dichloromethane. a) During the electrolysis at 1.00 V vs. Ag/Ag^+ at $-20^\circ C$; there are 10 mC intervals between two scans; b) the changes in the electronic absorption spectrum up to overall one electron transfer; c) the changes in the electronic absorption spectrum during the second electron transfer; d) the final spectrum obtained at the end of electrolysis and spectrum of free pyrazine; e) the changes in the electronic absorption spectrum of 8.80×10^{-5} M $Mo(CO)_5pz$ in dichloromethane during the electrolysis at 1.05 V vs Ag/Ag^+ at $-20^\circ C$. (There are 10 mC intervals between two scans); f) the electronic absorption spectrum of $[W(CO)_5pz]_2SO_4$ in dichloromethane prepared by chemical oxidation).

versus $\log V$ (Fig. 3), gave a negative slope for the first oxidation peak potential indicating a reversible electron exchange followed by a chemical reaction according to Nicholson-Shain criteria [23].

In the case of $Mo(CO)_5pz$ and $W(CO)_5pz$, the absence of the reduction peak accompanied to I_a could be due to the higher rate of chemical reaction, which is higher than the electron exchange rate. This is in accordance with the greater tendency of Mo and W to seven-coordination, in which any cation formed is more prone to nucleophilic attack. In case of $Cr(CO)_5pz$, the first oxidation peak is pseudo-reversible indicating the formation of relatively stable seventeen electron species as in the case hexacarbonyls of group 6B metals [24].

Spectroelectrochemistry

The change in the electronic absorption spectrum during the constant potential electrolysis at

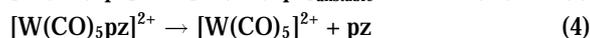
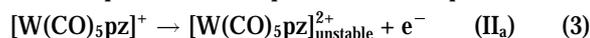
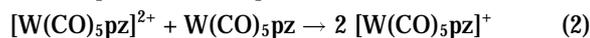
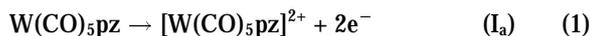
the first oxidation peak potential versus Ag/Ag^+ was followed in situ by UV-Vis spectroscopy in dichloromethane at $-20^\circ C$. The variations in the spectrum of $W(CO)_5pz$ are given as an example in Fig. 4. The band originally present at 242 nm split into two absorption bands at 234 and 250 nm and the intensity of all bands (Table 2) are observed to decrease during the course of electrolysis (Fig 4a). At the end of electrolysis, the band at 394 nm has shifted to 374 nm and a new band and a shoulder indicating the formation of free pyrazine ligand, appeared at 268 and 314 nm, respectively (Fig. 4d). The changes in the electronic absorption spectrum of the complex solution up to overall one electron transfer is shown in Fig. 4b. A close examination of the spectrum indicates the presence of three well defined isosbestic points at 262 nm, 298 nm and 327 nm. This suggests that only a one step electrode reaction is taking place in the electrolyte solution. Fig. 4c depicts the changes in the electronic absorp-

Table 2. Electronic absorption spectral data of the complexes in dichloromethane at room temperature.

Complex	λ_{\max} (nm)		
Cr(CO) ₅ Pz	243	400	516
Mo(CO) ₅ Pz	245	383	
W(CO) ₅ Pz	242	394	520

tion spectrum of the electrolysis solution during the second electron transfer. As seen from Fig. 4c formation of the band at 268 nm becomes more pronounced at this stage of electrolysis. A very similar behaviour was observed for the Mo(CO)₅pz complex as seen in Fig. 4e.

The controlled potential coulometry of W(CO)₅pz at the first oxidation peak potential indicates diffusion controlled two-electron transfer followed by a chemical reaction (Fig. 2 and 3). Thus, in the light of changes in the electronic absorption spectrum of the electrolysis solution and controlled potential coulometry, the following possible mechanism for the electrochemical oxidation of W(CO)₅pz, can be proposed:



According to this proposal, [W(CO)₅pz]²⁺ is formed in the first electrochemical step (I_a) after the two-electron transfer. [W(CO)₅pz]²⁺ then reacts with a neutral complex to form relatively more stable [W(CO)₅pz]⁺, or else, it may decompose to [W(CO)₅]²⁺ and free pyrazine in the subsequent chemical steps. The second electrochemical step corresponds to the oxidation of [W(CO)₅pz]⁺ to unstable [W(CO)₅pz]²⁺, which disproportionates to [W(CO)₅]²⁺ and pyrazine. The former, [W(CO)₅]²⁺, is not stable and decomposes to CO and W²⁺.

In fact, chemical oxidation of W(CO)₅pz was also studied by the addition of stoichiometric amount of (NH₄)₂S₂O₈ and I₂ in acetonitrile solutions, separately. During the chemical oxidation process by S₂O₈²⁻, the complex was oxidized to [W(CO)₅pz]⁺ and then precipitated as a brown sulphate salt, [W(CO)₅pz]₂SO₄. The electronic absorption spectrum of [W(CO)₅pz]₂SO₄, shown in Fig. 4f, is the same as the spectrum of the product that obtained at the end of first electrochemical and chemical step.

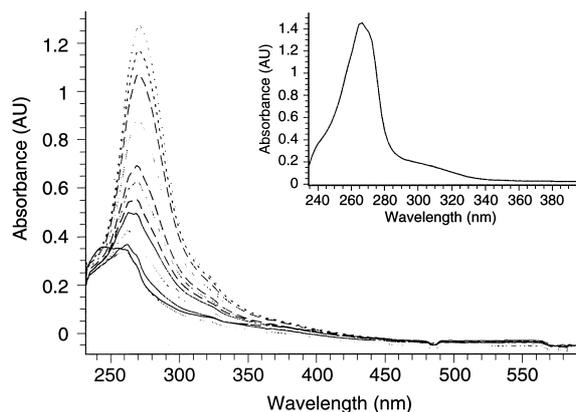


Fig. 5. The changes in the electronic absorption spectrum of 1.50×10^{-5} M W(CO)₅pz in dichloromethane during the electrolysis after second electron transfer; there are 5 mC intervals between two scans. Inset: The electronic absorption spectrum of pz⁺ obtained during the electrolysis of 1.60×10^{-4} M pyrazine in dichloromethane at 2.00 V vs. Ag/Ag⁺ at room temperature.

In the case of I₂ oxidation, monovalent cation complex was precipitated with BPh₄⁻ and its electronic absorption spectrum is also found to be very similar to that of the electrochemical product.

Coulometric measurements during the electrochemical oxidation process reveals that the production of the pyrazine becomes more significant during the second electron transfer. Upon prolonged electro-oxidation, the intensity of the band formed at around 262 nm increases rapidly and shifts to 268 nm (Fig. 5). This band is most probably associated with the production of cationic pyrazine. The same spectral changes were observed during the electro-oxidation of the pyrazine in dichloromethane which is given in the inset of Fig. 5. Decay of the cationic pyrazine was also monitored. The natural logarithm of the signal intensity, which is proportional to the concentration of species giving the signal, versus time plot (Fig. 6), obeys the first order kinetics and the half life of the intermediate was found to be 13 s.

In order to find out whether the HOMO of the complex is metal based or ligand based, the electrochemical oxidation of W(CO)₅pz was also carried out in the [(n-C₄H₉)₄BF₄]-dichloromethane electrolyte-solvent couple at low temperature (-40 ± 5 °C) inside the ESR resonator, using a quartz ESR-cell. The ESR spectrum is given in Fig. 7a. The g-value, measured with reference to DPPH was found to be 1.945, suggests the presence of the [W(CO)₅pz]⁺

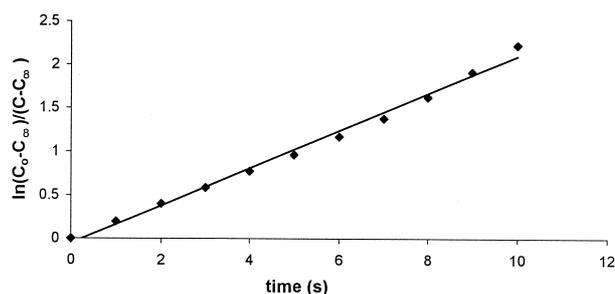


Fig. 6. Decay of the band formed at around 268 nm during the oxidation of $W(CO)_5pz$.

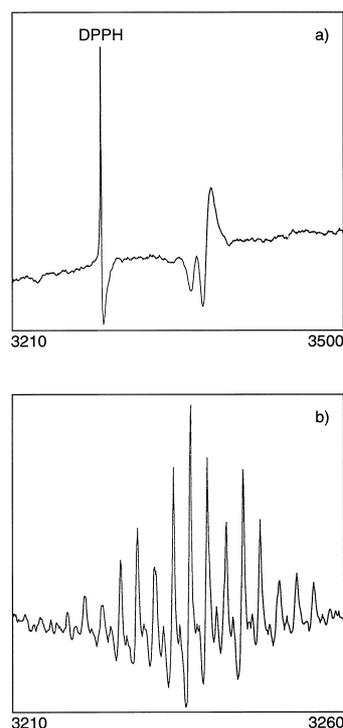


Fig. 7. ESR spectrum a) obtained during constant current electro-oxidation of $W(CO)_5pz$; b) obtained during constant current electro-reduction of $W(CO)_5pz$ in dichloromethane at 233 K.

complex cation. The electrochemical reduction of the complex was also carried out at constant current ($20 \mu A$) at $-40 \pm 5^\circ C$ in situ in the ESR-cell. During the electrochemical reduction, a quintet of triplets was observed (Fig. 7b). This spectrum is observed to be in good accordance with that of the pyrazine radical anion.

Conclusion

The electrochemical behaviour of $M(CO)_5pz$ [$M = Cr(0), Mo(0)$ and $W(0)$; $pz = pyrazine$] com-

plexes was studied by cyclic voltammetry. The first oxidation peak potentials in the voltammograms obtained for the chromium, molybdenum and tungsten complexes are 1.10, 1.30 and 1.30 V vs. SCE and 0.80, 1.05, and 1.03 V vs. Ag/Ag^+ , in dichloromethane at $-20^\circ C$, respectively. Coulometry experiments suggested that the oxidation process involves a metal-based two electron transfer reaction for $W(CO)_5pz$, which is followed by a chemical reaction according to the Nicholson-Shain criteria.

In order to identify the final products of the electrolysis, electrochemical oxidation of the complexes were followed in situ by UV-Vis spectroscopy at their first oxidation potentials. Well-defined isosbestic points appeared in all spectra indicating only one type of electrochemical reaction. In the case of $W(CO)_5pz$, $[W(CO)_5pz]^{2+}$ is formed after the first electrochemical step which is followed by a chemical step yielding $[W(CO)_5pz]^+$. Further oxidation of $[W(CO)_5pz]^+$ yields $[W(CO)_5pz]^{2+}$ which releases pz . Similar electrochemical mechanism is expected for $Cr(CO)_5pz$ and $Mo(CO)_5pz$ complexes.

In situ low temperature constant current ESR electrolysis confirmed the production of $[W(CO)_5pz]^+$ during the electrochemical oxidation. However, electrochemical reduction is found to be taking place over a pyrazine ligand based orbital instead a metal based one by producing $[M(CO)_5pz]^-$ which is also proved by ESR measurements.

A comparison of the first oxidation peak potentials suggest that the energies of the filled d-orbitals are the highest in the case of $Cr(CO)_5pz$ and the lowest in the case of $Mo(CO)_5pz$ and $W(CO)_5pz$.

Acknowledgements

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