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POLAROGRAPHIC BEHAVIOUR OF π-ALLYLIC COMPLEXES OF TRANSITION METALS

I. π-ALLYLIC DICARBONYLNITROSYLIRON COMPLEXES

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SUMMARY

The polarographic behaviour of π-$C_3H_5Fe(CO)_2NO$, π-$(1\text{-}CH_3C_3H_4)Fe(CO)_2NO$, π-$(2\text{-}CH_3C_3H_4)Fe(CO)_2NO$, π-$(1\text{-}ClC_3H_4)Fe(CO)_2NO$, π-$(2\text{-}ClC_3H_4)Fe(CO)_2NO$ and $(2\text{-}BrC_3H_4)Fe(CO)_2NO$ have been investigated in CH_3CN. Chemical (with $NaBH_4$) and electrochemical reductions, carried out on some of the above complexes have both been shown to follow the same pathway. On the basis of the results obtained a general reduction mechanism is proposed and discussed.

Effects of substituents on the mechanism and on the halfwave potentials has also been examined.

INTRODUCTION

In two previous papers the polarographic reduction of carbonylnitrosyl complexes of transition metals was described[1,2]. In all the complexes so far examined the number of electrons accepted by each molecule is equal to the number of nitrosyl groups, and the electronic change is localized on a molecular orbital with predominantly π^*_{NO} antibonding character. Nitrosyl complexes with organic ligands (*e.g.* cyclopentadiene) have also been studied[3]. In this case also, the electron change localisation is at the π^*_{NO} orbital, which accounts for the observation that the π-bonded organic ligands are unaffected by the reduction process[4].

We have now examined the complex π-$C_3H_5Fe(CO)_2NO$ and its methyl-, chloro- and bromo-allylic derivatives in order to ascertain how far the above observations can be applied to these complexes, and to evaluate the substituent effects on the nature of the reduction process. The only carbonyl allylic compounds previously investigated are the complexes π-$C_3H_5Fe(CO)_3X$ with $X = Cl$, Br, or I; with these the reduction proceeds with addition of one electron to the Fe–X bond, leading to its cleavage[5].

EXPERIMENTAL

π-$C_3H_5Fe(CO)_2NO$, π-$(1\text{-}CH_3C_3H_4)Fe(CO)_2NO$, π-$(2\text{-}CH_3C_3H_4)Fe(CO)_2NO$[6], π-$(1\text{-}ClC_3H_4)Fe(CO)_2NO$, π-$(2\text{-}ClC_3H_4)Fe(CO)_2NO$, π-$(2\text{-}BrC_3H_4)Fe(CO)_2$-

NO[7] and $(C_2H_5)_4N[Fe(CO)_3NO]$[8] were prepared and purified by literature methods. The solvent,CH_3CN, was purified by standard methods used in electrochemistry[9]. Owing to the air sensitivity of the compounds all the measurements were performed under argon. The stability of the complexes under these conditions was confirmed by infrared measurements. The supporting electrolyte, $(C_2H_5)_4N(ClO_4)$, was of chemically pure reagent grade.

Conventional polarographic measurements were carried out on an AMEL mod. 462 apparatus with a three-electrode cell arrangement; oscillograms were taken with a single sweep AMEL mod. 488 oscillographic polarograph. The measurements were made at room temperature (20±1°); the dropping mercury electrode had the following characteristic constant at -1.4 volts: $m^{2/3} \cdot t^{1/6} = 3.32$ mg$^{2/3}$·sec$^{-1/2}$. All the reported potential values are uncorrected for ohmic drops and refer to the saturated calomel electrode (SCE).

Infrared spectra were recorded on a Perkin–Elmer Model 521 apparatus.

Other experimental details are described in reference[2].

RESULTS AND DISCUSSION

(*a*). *Polarography*

π-$C_3H_5Fe(CO)_2NO$ exhibits two polarographic cathodic waves in CH_3CN (Fig. 1). The first, at -1.43 V, is a well defined diffusion wave: its limiting current is proportional to the depolarizer concentration (Fig. 2) and to the square root of the mercury height above the capillary ($\sqrt{h_{Hg}}$). The logarithmic analysis and oscillographic measurements show that reduction is an irreversible process. The comparison of the wave height with standard substances [as C_5H_5NiNO, $FeCO(NO)_2P(C_6H_5)_3$] and the coulometric reductions (see further) indicate that the wave is bielectronic.

The second wave, at -2.77 V, has a poor shape; its height cannot meaningfully be compared with that of the first wave, because the capillary drop time considerably changes at such negative potentials. For this reason this wave has not been studied in detail either by conventional or by oscillographic methods.

The addition of protogenic agents, such as perchloric acid, does not influence

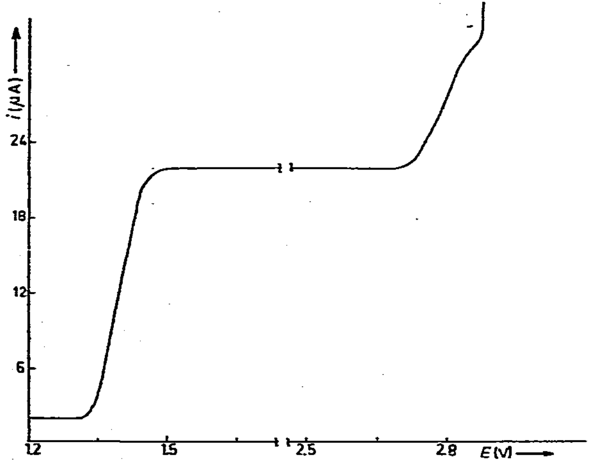
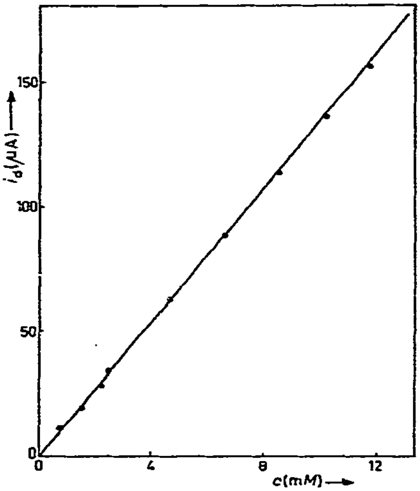


Fig. 1. Polarogram of π-$C_3H_5Fe(CO)_2NO$ in CH_3CN, $(C_2H_5)_4NClO_4$ 0.1 *M*. Potentials are referred to the SCE.



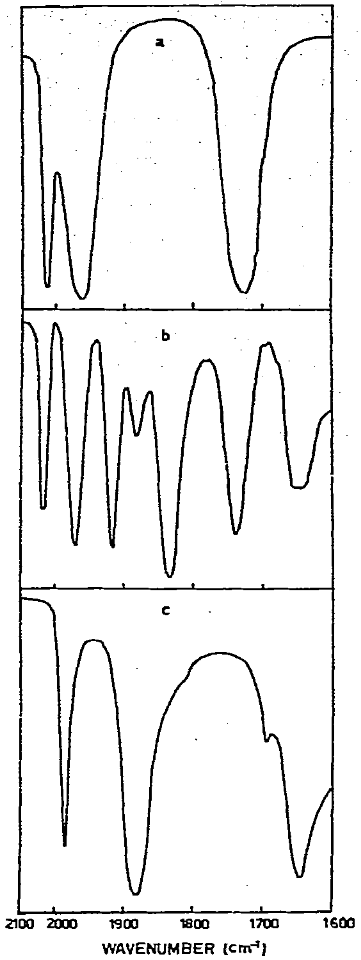


Fig. 2. Limiting current *vs.* concentration for the first wave of π-$C_3H_5Fe(CO)_2NO$, $(C_2H_5)_4NClO_4$ 0.1 *M*.

Fig. 3. Infrared spectra in the C–O and N–O stretching region during the chemical reductions of π-$C_3H_5Fe(CO)_2NO$ with $NaBH_4$ in CH_3CN: a, spectrum of π-$C_3H_5Fe(CO)_2NO$; b, spectrum after 3 min; c, final spectrum.

the first wave, while it more than doubles the limiting current of the second one. In order to explain these polarographic results, chemical and electrochemical reductions of concentrated solutions of the complexes were carried out.

(*b*). *Chemical reductions*

The chemical reductions were performed in CH_3CN using $NaBH_4$ as reducing agent. The reaction course was checked spectroscopically (Fig. 3). The following results were observed: the intensity of the carbonylic and nitrosylic bands of the complex π-$C_3H_5Fe(CO)_2NO$ (2033, 1968, 1736 cm^{-1}) (Fig. 3a) decreased progressively. An intermediate, characterised by the absorption frequencies 1914, 1832, 1653

cm^{-1}* (Fig. 3b), was formed initially. It reacted further producing a stable compound with bands at 1982, 1882, 1640 cm^{-1} and unstable products having absorptions in the nitrosylic stretching region only (1712, 1692 cm^{-1}) (Fig. 3c), which successively disappeared. During these reductions a gas developed which was found by IR analysis to be a mixture of propene and carbon monoxide. The stable compound was separated and identified as $Na^+[Fe(CO)_3NO]^-$ from its IR frequencies[10].

The chemical reductions of the allylic derivatives π-$(1\text{-}CH_3C_3H_4)Fe(CO)_2NO$, 1-Cl- and π-$(2\text{-}ClC_3H_4)Fe(CO)_2NO$ were also performed. The final product was again $Na^+[Fe(CO)_3NO]^-$ The intermediate was observed only in the reduction of the methyl derivative. Its IR bands coincide with those of the intermediate obtained in the π-$C_3H_5Fe(CO)_2NO$ reduction. This is convincing evidence that the intermediate does not contain the allylic group otherwise substituent effects on the nitrosylic and carbonylic bands would be found like those observed with the non reduced complexes [π-$C_3H_5Fe(CO)_2NO$: 2033, 1968, 1736 cm^{-1}; π-$(1\text{-}CH_3C_3H_4)Fe(CO)_2NO$: 2023, 1960, 1727 cm^{-1}].

We conclude that the intermediate can be formulated as $[Fe(CO)_2NO]^-$, the presence of the negative charge accounting for the rather low values of the CO and NO stretching frequencies.

(*c*). *Coulometric reductions*

Constant potential coulometric reductions of the complexes π-$C_3H_5Fe(CO)_2$-NO, π-$(CH_3C_3H_4)Fe(CO)_2NO$ and π-$(ClC_3H_4)Fe(CO)_2NO$ were undertaken at a mercury pool electrode on the plateau of the first wave. These reductions were periodically stopped so that the spectrophotometric and polarographic analyses could be carried out.

The IR spectra revealed the formation of intermediate and final products identical with those involved in the chemical reductions. This is convincing evidence that the chemical and electrochemical reductions proceed by the same mechanism.

The polarograms showed a gradual lowering of the first wave and the appearance of two anodic waves of similar height at −0.13 and +0.54 V respectively. These new waves are due to the oxidation of the $[Fe(CO)_3NO]^-$ ion formed by the depolarizer reduction, as confirmed by measurements carried out on the ionic complex $(C_2H_5)_4N^+[Fe(CO)_3NO]^-$[11]. The wave at −2.77 V, on the other hand, remained unchanged. The exhaustively electrolyzed solutions appeared turbid owing to the presence of suspended iron oxides.

The number of electrons, *n*, transferred in the reduction of π-$C_3H_5Fe(CO)_2NO$ is two until a small percent of complex has been reduced, and then tends towards one up to the electrolysis. The methyl derivatives behave similarly to the unsubstituted complex, whereas for the chloro complexes, *n* is one at the beginning of reduction and later rises, with increase in the proportion of reduced substance.

(*d*). *Reduction mechanism*

The results of the chemical and electrochemical measurements support the following mechanism.

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* The identification of the N–O stretching of the intermediate is uncertain owing to the overlap of its NO band with that of $[Fe(CO)_3NO]^-Na^+$.

$$\pi\text{-}C_3H_5Fe(CO)_2NO \xrightarrow{+2e} [Fe(CO)_2NO]^- + C_3H_5^-$$
$$\qquad\qquad\qquad\qquad \llcorner\!\xrightarrow{\text{solvent}} CH_3CHCH_2 \tag{1}$$

$$[Fe(CO)_2NO]^- + \pi\text{-}C_3H_5Fe(CO)_2NO \rightarrow$$
$$\rightarrow [Fe(CO)_3NO]^- + \text{unstable products} + CH_3CHCH_2$$
$$\qquad\qquad\qquad\qquad \llcorner\!\xrightarrow{\text{solvent}} CO + Fe^{2+} + NOH^- \tag{2}$$

$$2\,[Fe(CO)_2NO]^- \rightarrow [Fe(CO)_3NO]^- + \text{unstable products}$$
$$\qquad\qquad\qquad\qquad \llcorner\!\xrightarrow{\text{solvent}} CO + Fe^{2+} + NOH^- \tag{3}$$

The NO ligand does not participate in the reduction process, because in all the complexes for which the reduction is localized on this group the corresponding wave is monoelectronic. Instead, under the conditions of our experiments, reduction of π-$C_3H_5Fe(CO)_2NO$ is a bielectronic process and involves a cleavage of the Fe–allyl π-bond. This hypothesis is also supported by preliminary studies on the complex π-$C_3H_5Co(CO)_3$[11], which displays a bielectronic cathodic wave at a potential very close to that of π-$C_3H_5Fe(CO)_2NO$. Our results are in contrast with the conclusion reported by Gubin *et al.* according to which "the π-bonds of the iron atom with the allyl ligand are unaffected in the reduction"[5].

The addition of two electrons to the parent complex results, in our opinion, in the intermediate anion $[Fe(CO)_2NO]^-$ (see, chemical reductions). This intermediate reacts to give one molecule of the final product $[Fe(CO)_3NO]^-$ for every 2 molecules of the parent complex which disappears; the reactions (2) and (3) account for this experimentally-observed ratio. The lowering of n in the course of the coulometries points to a reaction between the parent complex and the intermediate product of reduction[13] [eqn. (2)]. In fact, infrared kinetic controls carried out on partly reduced solutions showed a gradual decrease of the depolarizer concentration until the intermediate was completely exhausted.

It has also been observed that at the end of the coulometric reductions the formation of $[Fe(CO)_3NO]^-$ proceeds further until all the accumulated intermediate has disappeared. This observation supports reaction (3) and provides further evidence that the electronic change is not localized on the Fe–NO bond. In fact, the breaking of the Fe–NO bond should produce an intermediate, $[C_3H_5Fe(CO)_2]$, which, by reaction (3), would not be able to give rise to the formation of $[Fe(CO)_3NO]^-$ anion.

The two competitive reactions (2) and (3) proceed with comparable rates. In the halogen-substituted derivatives the intermediate was not observed. This fact and the coulometric value of n ($=1$)[12], indicate that the rate of reaction (2) is much larger than the rate of the corresponding reaction for the π-$C_3H_5Fe(CO)_3NO$ complex and than of the reaction of type (3).

At the potential of the second wave the complex $[Fe(CO)_3NO]^-$ is reduced. Probably, at the same potential, the species, containing NO (NOH^-)[1,2], formed in the dismutative processes (2) and (3), are also reduced. The simultaneous reduction of $[Fe(CO)_3NO]^-$ and NOH^- could be a possible explanation of the observed height of this wave.

TABLE 1

HALF-WAVE POTENTIALS ($E_{\frac{1}{2}}$) IN CH_3CN OF SOME DERIVATIVES OF π-$C_3H_5Fe(CO)_2NO$

Compounds	$E_{\frac{1}{2}}$ (V)
π-$C_3H_5Fe(CO)_2NO$	−1.43
π-(1-ClC_3H_4)$Fe(CO)_2NO$	−1.16
π-(1-$CH_3C_3H_4$)$Fe(CO)_2NO$	−1.50
π-(2-ClC_3H_4)$Fe(CO)_2NO$	−1.10
π-(2-BrC_3H_4)$Fe(CO)_2NO$	−1.31
π-(2-$CH_3C_3H_4$)$Fe(CO)_2NO$	−1.63

(*e*). *Substituent effects*

In Table 1 the half-wave potentials of the first wave of all the investigated compounds are collected. The introduction of substituents on the allylic group does not change the character of the reductive process, but the $E_{\frac{1}{2}}$ value considerably depends on the nature or position of the substituent. Electron-releasing substituents, *i.e.* $-CH_3$, which increase the electronic density on the Fe–allyl bond, shift the reduction potentials toward more negative values. Electron-attracting substituents (Cl, Br), on the other hand, increase the ease of reduction.

It should be noted that substituents in position 2 influence $E_{\frac{1}{2}}$ more than those in position 1, as observed in kinetic measurements on the substitution reactions with phosphinic ligands on the $C_3H_5Co(CO)_3$ complex and its allylic derivatives[13]. In our opinion, this is due to the larger influence on the Fe–allyl bond of the substituents in position 2 compared with those in position 1.

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