Electrochemical Behaviour of Dinitrosylbis(triethyl phosphite)-cobalt(I) Tetraphenylborate in Acetonitrile

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The electrochemical behaviour of the complex $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$ has been studied in acetonitrile, using platinum and mercury electrodes. It undergoes two subsequent reduction processes and a single oxidation process. In particular, the less cathodic one-electron reduction leads to the formation of the corresponding neutral species which is fairly stable in carefully deaerated solution.

As a part of our studies dealing with the electrochemical properties of nitrosyl cobalt complexes,[1,2] we report here on the voltammetric behaviour of the dinitrosylcobalt complex $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$ in acetonitrile. The aim of this investigation was that of studying the capabilities of the electrochemical methods in preparing nitrosyl cobalt compounds in unusual oxidation states and of elucidating the nature of the underlying electrode mechanisms.

Experimental

Materials and apparatus employed, as well as the procedure followed, have been described before.[1] Infrared spectra were recorded with a Perkin-Elmer model 683 spectrophotometer and e.s.r. spectra were obtained with a Varian E3 spectrometer operating at 9.45 GHz, electrogenerating the species directly within the cavity. The manipulation of the electrolysis products was performed in an argon atmosphere within a dry-box.

Results and Discussion

Figure (*a*) shows the cathodic portion of the voltammetric picture exhibited by a MeCN solution of $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$ at a mercury working microelectrode. Two subsequent cathodic processes are shown; to the less cathodic peak a directly associated anodic one is recorded (cathodic-anodic peak system A–B), while to the more cathodic peak C no anodic peak is associated.

Controlled potential coulometric tests at the potentials of peak A led to a consumption of one mol of electrons per mol of starting compound. The values of the parameters of the cyclic voltammetric curves recorded at potential scan rate, v, ranging from 0.05 to 100 V s^{-1}, allowed us to establish the reversible character of the one-electron charge transfer on the mercury electrode, while some irreversibility degree had to be attributed to the charge transfer occurring at a platinum electrode; the reproducibility of the response suggests disregarding the occurrence of electrode poisoning. The different reversibility degrees of the charge transfer on different electrode materials suggest that the heterogeneous redox process occurs *via* an inner-sphere mechanism.[3]

Voltammetric tests on the solution exhaustively electrolyzed at peak A showed the presence of the reduced form of the redox couple involved in the peak system A–B shown in Figure (*a*). The i.r. spectrum of this solution showed only two bands in the NO stretching region, at 1 613 and 1 690 cm^{-1}. They are shifted *ca.* 200 cm^{-1} compared to those of the starting complex [ν(NO) at 1 811 and 1 869 cm^{-1}]. Although the solution was paramagnetic, as checked by the Evans' method,[4] no e.s.r. signal was detectable at room temperature.

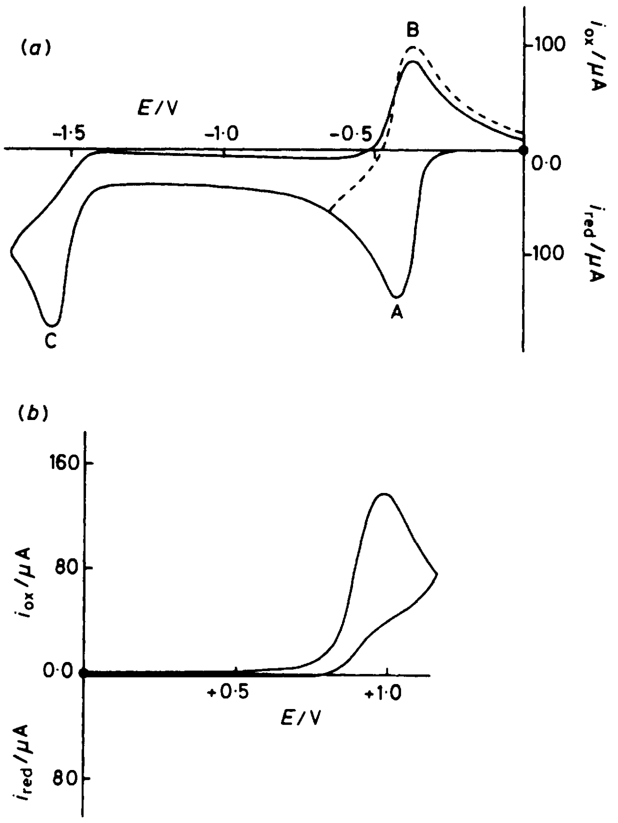
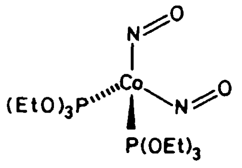


Figure. Cyclic voltammetric curves recorded on a MeCN solution containing 3.5×10^{-3} mol dm^{-3} $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$ and 0.1 mol dm^{-3} $[NEt_4][ClO_4]$; scan rate 0.2 V s^{-1}; ● is the starting potential. (*a*) Mercury working microelectrode, cathodic scan, and (*b*) platinum working microelectrode, anodic scan; saturated calomel reference electrode (s.c.e)

We were not able to isolate the reduced species in pure form, owing to its instability. The i.r. spectrum of the solid resulting from the electrolyzed solution exhibited, in addition to the bands at 1 613 and 1 690 cm^{-1}, the absorptions due to the presence of the starting species $[Co\{P(OEt)_3\}_2(NO)_2]^+$.



(I)

Furthermore, by exposing the reduced solution to the air the same cationic species was regenerated in an almost quantitative yield (≥90%). This is not surprising, in view of the low potential value at which the reduction product is reoxidized.

On the basis of the data reported above the one-electron reduction of the complex $[Co\{P(OEt)_3\}_2(NO)_2]^+$ should lead to the formation of the corresponding neutral compound $[Co\{P(OEt)_3\}_2(NO)_2]$, in which both the tetrahedral geometry and the co-ordination of the starting complex is retained (see below).

$$[Co\{P(OEt)_3\}_2(NO)_2]^+ + e^- \rightleftharpoons [Co\{P(OEt)_3\}_2(NO)_2]$$

An $E_{\frac{1}{2}}$ value of −0.39 V *vs.* s.c.e. could be evaluated for this redox couple.

Moreover the observed lowering of the ν(NO) frequencies in the neutral species compared the cationic starting compound seems to suggest that the higher electron density due to the one-electron reduction should be distributed over the $Co(NO)_2$ moiety, with a probable change in the MNO angle from linear to slightly bent [see (I)].[5,6]

As far as the peak C is concerned, from cyclic voltammetric tests at different v it could be concluded that on the voltammetric time-scale the more cathodic process consists of a reversible one-electron charge transfer followed by a fast irreversible chemical reaction (absence of any associated anodic peak also at the highest potential scan rate, shift of the peak potential for a ten-fold increase in v always equal to −30 mV, difference between half-peak and peak potential lower than 60 mV, constant current function, almost equal to that of the less cathodic peak). Accordingly, electroreducing at peak C solutions previously electrolyzed at peak A, one further mol of electrons was consumed; on the other hand, performing the electrolysis at peak C directly on solutions of the starting complex, the current reached the background value after consuming two mol of electrons per mol of cobalt compound. These solutions contained rather small amounts (≃30%) of the mononitrosyl compound $[Co\{P(OEt)_3\}_3(NO)]$,[1] together with paramagnetic species without any nitrosyl ligand. The presence of these species does not provide clear information on the nature of the chemical reaction which the two-electron reduction product undergoes.

Figure (*b*) shows the anodic behaviour exhibited by a MeCN solution of $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$ at a platinum electrode. A single anodic process is observed and no cathodic peak is recorded in the reverse scan before reaching the reduction of the starting compound.

Controlled potential electrolyses at +1.25 V led to a consumption of four mol of electrons per mol of starting compound. The resulting solution showed a marked acidic character.

The cyclic voltammetric response has been analysed at v ranging from 0.05 to 100 V s^{-1}, and compared with that relative to the reversible one-electron oxidation of bis(cyclopentadienyl)iron(II) under the same experimental conditions. The extent of the peak potential shift at varying v, the value of the difference between peak and half-peak potentials, and the value of the current function are all consistent with a two-electron irreversible oxidation, the first electron being transferred in the slower step,[7] characterized by a value of 0.45 ± 0.03 for the charge-transfer coefficient, α.

The fact that the anodic oxidation is a two-electron process on the voltammetric time-scale suggests that a slow chemical reaction must precede the further release of two electrons. Since the electrolysis product recovered showed that no nitrosyl cobalt complex was present, it can be suggested that the NO ligand is released quantitatively. Taking into account that free nitrogen oxide, NO, is oxidized to NO^+ at the electrolysis potentials,[8] and that NO^+ undergoes a hydrolysis reaction leading to H^+ ions and HNO_2 with water still present, even if at small levels, in the acetonitrile solvent, both the coulometric results and acidic character of the electrolyzed solution can be explained.

Acknowledgements

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References

1 R. Seeber, G. A. Mazzocchin, G. Albertin, and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1980, 979.
2 G. Albertin, E. Bordignon, G. A. Mazzocchin, A. A. Orio, and R. Seeber, *J. Chem. Soc., Dalton Trans.*, 1981, 2127.
3 I. B. Kravtsov, *J. Electroanal. Chem.*, 1976, **69**, 125.
4 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
5 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.
6 R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, 1974, **13**, 2666.
7 M. D. Ryan, *J. Electrochem. Soc.*, 1978, **125**, 547.
8 G. Bontempelli, G. A. Mazzocchin, and F. Magno, *J. Electroanal. Chem.*, 1974, **55**, 91.

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