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Polarographic Studies of Nitrosyl Compounds. VIII.* Reduction of Substituted $Co(CO)_3NO$ Complexes in THF

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Reduction of a series of complexes derived from $Co(CO)_3NO$ in which one or two carbonyl groups were substituted by other ligands was studied polarographically. It was found that in all cases the complexes are reduced reversibly to the radical anion which is irreversibly inactivated. The rate of the inactivation is comparable within the series studied so that the measured changes of half-wave potentials correspond to changes of standard redox potentials. A correlation of these quantities with the N–O stretching frequencies indicates a considerable degree of delocalization of the redox orbital.

Introduction

From the point of view of the redox reactivity of coordinated nitrosyl group the series derived from $Co(CO)_3NO$ is interesting because the change of the electron density on the ligand NO results only as a secondary effect from substitution of the CO group by other π-accepting ligands. The aim of the present study was to establish to which extent the substitution affects the mechanism of the electrode reaction and its quantitative parameters. A similar series of compounds was studied by other authors[1] in acetonitrile, dimethylformamide (DMF) and partially also in dimethylsulfoxide (DMSO). The authors state that the polarographic behaviour of $Co(CO)_3NO$ in aprotic DMSO considerably differs from that observed in slightly protogenic CH_3CN and DMF. In order to ascertain a strictly aprotic medium our study was performed in tetrahydrofuran (THF). The complexes studied were: $Co(NO)(CO)_3$ (I), $Co(NO)(CO)_2P(C_6H_5)_3$ (II), $Co(NO)(CO)_2 As(C_6H_5)_3$ (III), $Co(NO)(CO)[As(C_6H_5)_3]_2$ (IV), $Co(NO)(CO)_2 P(p\text{–}CH_3OC_6H_4)_3$ (V), $Co(NO)(CO)[P(p\text{–}CH_3OC_6H_4)_3]_2$ (VI), $[Co(NO)(CO)_2]_2$diphos (VII) and $Co(NO)(CO)$diphos (VIII), where diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

Experimental Section

Polarographic measurements were carried with polarographs LP-60 (Laboratory Instruments, Praha) and OH-102 (Radelkis, Budapest) enabling the IR-compensation. The mercury dropping electrode used had the following characteristics: the outflow velocity of mercury m = 1.69 mg/s and the drop-time t_1 = 3.1 s at the height of the mercury column h = 60 cm at the potential −1.0 against the normal calomel electrode (NCE).

In oscillopolarographic measurements (function dE/dt −E) the Polaroscope P 576 (Krizík, ZPA, Praha), and the streaming mercury electrode according to Woggon and Spranger[2] were used. Platinum wire spiral served as a reference electrode.

The commutator of the polarizing voltage according to Kalousek[3] worked in the frequency range 1.5-25 c/s.

The electrode potential was measured by means of the QTK-Compensator (Metra, Blansko) and the solution resistance by means of the Wheatstone bridge OK 102 (Radelkis, Budapest) working with the frequency 80 c/s and 3 kc/s.

Polarographic measurements were carried out in H-cell or in Kalousek vessel provided with ground joints. As reference electrode in anhydrous THF the separated mercury bottom with 0.1 *M* Bu_4NClO_4 in THF was used. In some cases aqueous silver chloride electrode connected with the investigated solution my means of the bridge containing 0.1 *M* Bu_4NClO_4 in THF served as reference electrode.

All operations during the work with non-aqueous THF were carried out in inert atmosphere using the securation method with the corresponding instrumentation.[4] Nitrogen and argon which served as inert gases were made free of traces of oxygen and dried by passing the gas through columns filled with the BTS catalyst (BASF, Ludwigshafen), molecular sieve Calsit 5 and phosphorus pentoxide.

All commercial chemicals used, unless otherwise stated, were Lachema p.a. purity grade products.

The tetrahydrofuran (E. Merck A.G., Darmstadt) was purified prior to use by the method of ketyl drying.[4,5] The glass assembly in which the THF was refluxed enabled us to distill the purified, deoxygenated and dry THF into the polarographic vessel previously securated.

$CoNO(CO)_3$ (I) prepared[6] at the Technical University in Veszprém was purified prior to use by

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(*) Part VII. This Journal *4*, 175 (1970).

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distillation *in vacuo* and stored in sealed ampoules under nitrogen atmosphere.

$Co(NO)(CO)_2P(C_6H_5)_3$ (II) was prepared by the reaction of (I) with $P(C_6H_5)_3$ in toluene. The product was precipitated by addition of methanol.[7,8] The composition of the compound was tested by the elemental analysis (C, H, N) and IR spectra.

The remaining complexes III-VIII were prepared at the Northwestern University, Evanston, Illinois by methods described in literature.[9,10] Their identity was tested by the elemental analysis.

Results

All the complexes mentioned in the experimental section were studied in the medium of anhydrous THF with Bu_4NClO_4 as supporting electrolyte and showed an analogous polarographic behaviour. The complexes (I) to (VI) and (VIII) containing one nitrosyl group are reduced in a single one-electron, diffusion controlled wave. The diphosphine complex (VII) containing two NO groups is reduced in a 2-electron diffusion controlled wave.

The number of electrons consumed in the reduction was determined by comparing the limiting diffusion corrents with those of the complex $[C_6H_5Fe(CO)_2]_2$ which yields a single 2-electron reduction wave[11] and $[(C_6H_5{-}C_6H_5)_2Cr]I$ which is reduced in a single 1-electron wave.[12]

The diffusion character of the limiting currents was proved by the dependence of the mean limiting current on the height of the mercury column (linear plot $i_l \sim \sqrt{h}$ pointing to the origin), by the dependence of the instantaneous current on time (linear plot $\log i \sim \log t$ with the slope aprox. 0.2) and by the temperature coefficient of the limiting current (1.6 - 1.7%/C°).

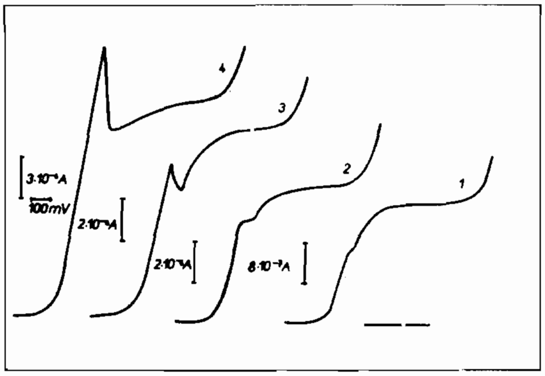

Figure 1. Polarographic Waves of $Co(NO)(CO)_2P(C_6H_5)_3$ at Various Depolarizer Concentrations; supporting electrolyte: 0.1 *M* Bu_4NClO_4 in THF. Depolarizer concentrations: (1) 2.5×10^{-4} *M*; (2) 7.0×10^{-4} *M*; (3) 9.4×10^{-4} *M*; (4) 1.77×10^{-3} *M*.

The polarographic waves are distorted by the presence of a maximum appearing on the ascending portion of the wave. At low concentrations of the depolarizer the maximum is not distinct and simulates an apparent separation into two waves or influences the steepness of the ascending part of the wave before reaching the half-wave potential (Figure 1). With higher concentrations of the depolarizer the maximum gets more pronounced till at concentrations above 1.5×10^{-3} *M* it is distinctly higher than the limiting curent. The maximum cannot be suppressed in the medium of non-aqueous THF by usual surface active substances. The height of the maximum is dependent on the rate and direction of the potential sweep: it decreases with decreasing rate of the sweep and disappears or is strongly depressed when the sweep is applied from negative towards positive potential values. After reaching the maximum the current decreases to a normal diffusion controlled value still at the ascending part of the wave which is a typical behaviour of the negative maxima of the first kind.[13] When the polarization sweep is stopped at the potential of the maximum the current changes as a function of time as shown in Figure 2. This behaviour was observed in aqueous media with maxima of nickel, zinc, cobalt and thallium.[14] At the potential of the maximum a strong streaming of the electrolyte in the direction from the neck of the drop is observed which is a characteristic feature at the negative maxima of the first kind. Addition of water up to 1% to the non-aqueous solution does not influence the height and the potential of the maximum. All these experimental findings including the time course of the instantaneous current in the potential region of the maximum point to the conclusion that the maxima acompanying the reduction of the studied complexes in THF medium are analogous to the streaming ones

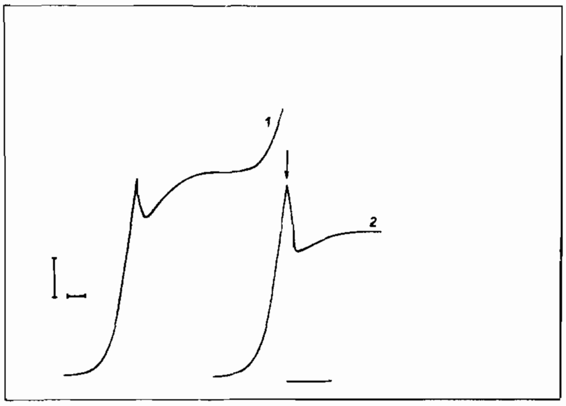

Figure 2. Properties of the Maximum on the Wave of $Co(NO)(CO)_2P(C_6H_5)_3$; supporting electrolyte 0.1 *M* $(Bu)_4NClO_4$ in THF; depolarizer concentration 1.26×10^{-3} *M*. (1) normally recorded curve; (2) the arrow indicates the point at which the potential scan is stopped and the current is recorded further as a function of time at constant potential.

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observed in aqueous media and are not caused by catalytic reactions or some other change of the reaction mechanism.

The reversibility of the electrode process was studied by means of the Kalousek commutator at the commutating frequency 25 c/s. All complexes studied show a closely similar behaviour. At room temperature the commutated curve represents a cathodic-anodic wave with the half-wave potential identical with that of of non-commutated cathodic wave. However, the anodic limiting current is only a small fraction of the cathodic part of the wave as shown in Figure 3, curve 2. With decreasing temperature of the solution the anodic part increases till at −18°C its height surpasses that of the cathodic limiting current (Figure 3, curve 5). Even at low temperature, however, the anodic part represents only about 1/7 of the anodic current expected for the reversible process (with simple reversible processes it is found experimentally that the anodic part of the wave at the commutator frequency 25 c/s is about 8 times as high as the cathodic limiting current). The mutual ratio of the anodic and cathodic part of the commutated wave at a given temperature is similar with all the complexes studied.

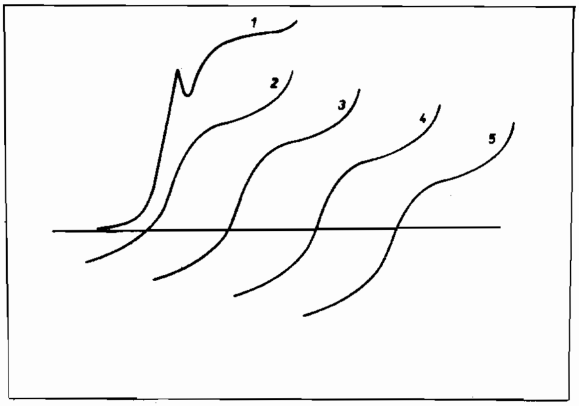

Figure 3. Influence of Temperature on Curves of Co(NO)-$(CO)_2P(C_6H_5)_3$ Obtained with the Commutator Method; supporting electrolyte: 0.1 *M* Bu_4NClO_4 in THF; depolarizer concentration 9×10^{-4} *M* f = 25. c/s; (1) normal i E curve; (2)-(5) commutated curves at temperatures +22°, +10°, 0° and −10°C, respectively.

To check the reversibility of the electrode process also the oscillopolarographic method (function dE/dt−E, controlled A.C. of 50 c/s, mercury streaming electrode, iR drop compensation) was used. All the complexes studied show a reversible cathodic and anodic incision at potentials corresponding to the polarographically found half-wave potentials.

The half-wave potentials measured against the separated mercury bottom electrode with 0.1 *M* Bu_4NClO_4 in THF are listed in Table I together with the N−O stretching frequencies taken from literature. In Figure 4 the correlation is shown between ν_{N-O} and $E_{1/2}$ for complexes studied in the present paper in THF on the one hand and those studied by other authors[1] in acetonitrile on the other hand. The $E_{1/2}$ values obtained in acetonitrile were formally recalculated to get agreement with the value for the complex I obtained in THF.

Table I. N−O Stretching Frequencies and Half-Wave Potentials of $Co(NO)(CO)_3$ and its Derivatives

Compound	N−O cm^{-1}	$E_{1/2}$ ^{a}, v
$Co(NO)(CO)_3$	1760 $^{d,\ e}$	−1.277
$Co(NO)(CO)_2P(C_6H_5)_3$	1806 ^{c,d}	−1.744
$Co(NO)(CO)_2As(C_6H_5)_3$	1765 $^{d,\ e}$	−1.470
$Co(NO)(CO)[As(C_6H_5)_3]_2$	1723 $^{d,\ e}$	−2.073
$Co(NO)(CO)_2P(p\text{—}CH_3OC_6H_4)_3$	1748 ^{f}	−1.778
$Co(NO)(CO)[P(p\text{—}CH_3OC_6H_4)_3]_2$	1687 ^{g}	−2.147
$[Co(NO)(CO)_2]_2$(diphos) ^{b}	1759 ^{h}	−1.787
Co(NO)(CO)(diphos) ^{b}	1712 ^{h}	−2.225

[a] $E_{1/2}$ *vs.* separated Hg-bottom with 0.1 Bu_4NClO_4 in THF. [b] diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [c] From A. A. Blanchard, J. R. Rofter, and W. B. Adams, *J. Am. Chem. Soc.*, *56*, 16 (1934). [d] From W. Beck and K. Lottes, *Ber.*, *98*, 2657 (1965). [e] From W. Hieber and J. Ellermann, *Ber.*, *96*, 1643 (1963). [f] From ref (9). [g] From E. M. Thornsteinson and F. Basolo, *Inorg. Chem.*, *5*, 1691 (1966). [h] From ref. (10).

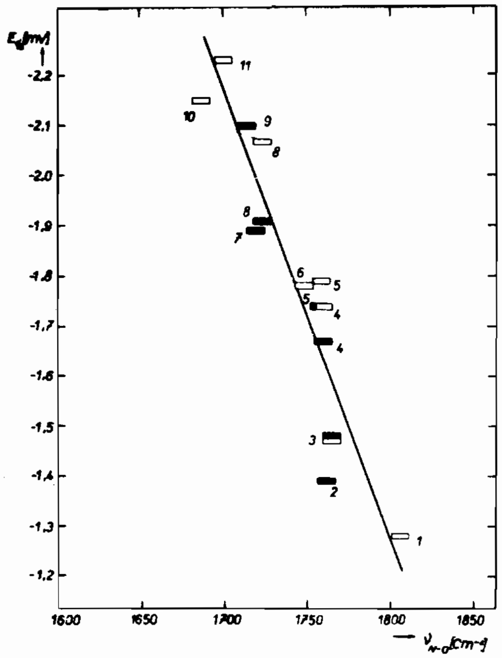

Figure 4. Correlation between $\nu_{N\text{-}O}$ and $E_{1/2}$ of $Co(NO)(CO)_3$ Derivatives; ▭ denote points obtained in THF in the present work; ▬ denote points obtained in CH_3CN (Ref. 1) recalculated to get agreement in the point 1 with the value obtained in THF; (1) I; (2) $Co(NO)(CO)_2Sb(C_6H_5)_3$; (3) III; (4) II; (5) VII; (6) V; (7) $Co(NO)(CO)[Sb(C_6H_5)_3]_2$; (8) IV; (9) $Co(NO)(CO)[P(C_6H_5)_3]_2$; (10) VI; (11) VIII.

Discussion

From oscillopolarographic and commutator experiments it follows that all the complexes studied are reduced reversibly (complexes containing one nitrosyl group with the uptake of 1 electron) under formation of an unstable primary product (probably Co-$(NO)(CO)_2L^-$) which is rapidly inactivated against reoxidation. The elucidation of the chemical nature of this inactivation reaction in the medium of the anhydrous THF is not simple and needs a further study.

The half-wave potentials given in Table I are influenced by the inactivation reaction according to the equation[15]

$$E_{1/2} = E^{\circ} + \frac{RT}{nF} \ln 0.886 \sqrt{[(D_{Ox}/D_{Red}) \, . \, kt_1]}$$

where k is the rate constant of the inactivation reaction and t_1 the drop-time. However, in view of the experimental finding that the ratio of the cathodic and anodic limiting current in the commutator curve at a given temperature is essentially the same for all the complexes studied, it can be assumed that the second right-hand term in the above equation represents within the series of the complexes studied a constant additive magnitude so that the changes in the half-wave potentials observed within this series are directly equal to the changes of the standard potential between the individaul redox couples. Due to the closely related structure of the complexes studied it can be expected that the entropy, solvation energy and configuration changes accompanying the primary electrode process are practically constant within the series. Hence it follows that the measured changes of the half-wave potential values represent quantities directly corresponding to electron affinity changes of the orbital into which the electron is accepted. The observed shift of the half-wave potentials towards more negative potential values with decreasing stretching frequency of N—O indicates that the main factor by which the substitution influences both these quantities is the electron density on the N—O bond.

A discussion of the correlation between ν_{N-O} and $E_{1/2}$, and of the degree of delocalization of the molecular redox orbital following from this correlation is given elsewhere.[16] This discussion is based on a simplified model according to which the changes in the N—O stretching frequency are prevailingly due to different degree of back-donation (resulting from a competition between different π-accepting ligands in the individual complexes) into the π*—MO of the NO group which is at the same time a significant component of the redox orbital. Recent calculations show[17,18] that in ligands of the isoelectronic type CO, N_2 (this applies presumably also to NO^+) the bond strength must be influenced significantly also by the sigma L→M donation (the highest occupied σ orbital of the ligand being slightly antibonding) and that electronic charge in the π*—NO orbital does not exert a significant bond-weakening force. These results apply, however, only in going from the free ligand to a complex, and in the free ligand system, respectively. Within a series of structurally related complexes studied in the present paper the amount of σ orbital occupation can be considered to remain essentially constant so that the change in physical observables such as stretching frequencies can be interpreted on the basis of π*—orbital participation. This conclusion is supported by recent calculations on seven pentacyanonitrosyl complexes in which the σ—occupation of NO^+ was found to be essentially constant[19] even if the changes of the π back donation within this series were much more drastic than within that studied in the present paper. This is in agreement with the experimental correlation in Figure 4 which shows the basic validity of the simple model in interpretation of this dependence and its observed trend.

Here it is to be emphasized that the correlated quantities, $E_{1/2}$, E°, E_j and ν_{N-O}, are physical parameters the mutual relation of which can be interpreted only through the electronic structure of the compounds. On the other hand, the relations between these physical observables and the electronic structure are rather complicated so that any model used in such correlations must involve certain simplifying assumptions the applicability of which can be proved only by the degree of observed agreement with experimental data similarly as is the case in quantum chemical calculations of the electronic structure. The most serious approximation in the model used for interpretation of the mentioned correlation is the « rigid orbital hypothesis »[18,20] which definitely does not hold in case of the change of the electron number by unit in the free ligand (NO^+—NO) but which may reasonably well apply in case of partial delocalized electron density transfer via the π back donation in the complex. It appears that coordination of the NO^+ group to a bulky transition metal complex stabilizes all the NO^+ levels and in particular places the σ donating level well below the metal d-orbitals and the corresponding σ donating orbitals on the CO groups.[19] This low lying σ—NO^+ level will remain essentially unperturbed by replacing a CO group by L. On the other hand, the antibonding π-orbital of NO^+ will be substantially lower than its CO counterpart and will be very sensitive to the σ donating and π-acceptor ability of the ligand L which is in agreement with our experimental observations.

Our experimental results differ in some aspects from those obtained by Piazza *et al.*[1] in CH_3CN, DMF and DMSO for a similar series of complexes. The main difference concerns the reversibility of the electrode reduction. On the basis of cyclic voltammetry performed with the hanging drop mercury electrode the authors claim a total irreversibility of the electrode process whereas from our experiments it follows that the primary reduction is reversible and is followed by an irreversible inactivation of the primary reduction product. In the paper[1] the scan rate of the cyclic voltammetry is not indicated but unless it was rather high (the half-life period of the primary products can be estimated from our measurements to be of the order of 10^{-2} s) it is evident that the reversible re-oxidation could not be detected in this way.

In the mentioned paper[1] an adsorption wave is described following the wave corresponding to the reduction wave of the free depolarizer. According to

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our orientation experiments performed in CH_3CH with the complex II and to our experience with the maxima showing up also in THF medium it appears that the separation of the « adsorption » wave is simulated by the occurence of a maximum on the ascending part of the wave as described in the Experimental part. A third wave occurring in the slightly protogenic CH_3CN and DMF is absent in aprotic DMSO which is consistent with our results in aprotic THF.

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