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Polarographic Studies of Nitrosyl Compounds. VII.* Reactivity of the $Mn(CN)_5NO^{3-}$ Ion

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It was found that the complex anion $Mn(CN)_5NO^{3-}$ hitherto considered as polarographically inactive can be reduced at the mercury dropping electrode in presence of excess of Cs^+ ions. This reaction is studied and its mechanism described.

Introduction

The complex anion $Mn(CN)_5NO^{3-}$ is a member of the isoelectronic series of complexes derived from the nitroprusside ion. $K_3[Mn(CN)_5NO] . 2H_2O$ is a violet crystalline substance with diamagnetic properties, stable on air for unlimited time when stored in darkness or diffusion light. Aqueous solutions of $K_3Mn(CN)_5NO$ are stable for several days and in absence of oxygen are not affected by alkali hydroxides up to 6 *M* concentration. In presence of air in alkaline media a slow decomposition of the complex under formation of MnO_2 occurs. By the action of acids such as HCl, $HClO_4$, H_2SO_4, H_3PO_4 the solution turns red which is caused by the reversible formation of protonated forms the pK values of which are[1] $pK_1 = 3.02$, $pK_2 = 3.32$, $pK_3 = 3.80$.

The complex is not reduced by reducing agents such as sulphurous acid and $SnCl_2$ but is readily oxidized[2,3] by HNO_3, Br_2, Cl_2, $KMnO_4$ to the complex $Mn(CN)_5NO^{2-}$ which forms yellow solutions. The standard potential of the reaction $Mn(CN)_5NO^{2-} + e \rightleftarrows Mn(CN)_5NO^{3-}$ amounts to[3] +0.597 against normal calomel electrode.

There are very scarce data on the electrochemical behaviour of the compound in the literature. The polarographic method was applied for the study of the photolytic decomposition of the complex which yields Mn^{2+}, CN^- and NO as products.[4] The authors state that the starting complex is polarographically nonreducible. The same conclusion is arrived at also by other authors.[5]

We found, however, that in presence of caesium salts the complex $Mn(CN)_5NO^{3-}$ is polarographically reduced at highly negative potentials. The aim of the present paper was to study these depolarization effects and to suggest a corresponding reaction mechanism which could be correlated with other members of the isoelectronic series.

Experimental Section

In the polarographic work the polarograph Radelkis Type OH−102 was used. The mercury dropping electrode had the following characteristics: the outflow velocity 1.05 mg/s, drop-time $t_1 = 3.1$ s at a height of the mercury column of 60 cm in 0.1N−KCl at the potential 0.0 V *vs.* normal calomel electrode (NCE). The construction of the polarographic vessel enabled us to carry out also electrolyses at the large-area mercury electrode. These electrolyses were carried out using a potentiostat constructed in the Institute workshop.

Electrolyses at the mercury dropping electrode were carried out in a micro-cell with mercury bottom of the volume 50 ml. For pH measurements the pH meter Radiometer PRM−4c with a glass electrode of the Type 6200 B was used. Instantaneous currents were recorded photographically with the use of the string galvanometer Kipp en Zonen (Holland). The hanging drop equipment was Metrohm, Herisau, make.

Quantitative determination of ammonia evolved in the electrolyses was carried out in the following way. In the course of electrolysis a stream of argon was passed through the solution and ammonia contained in the gas was trapped in a cooled solution ion of 0.01−HCl. When the electrolysis was finished the electrolytic vessel was heated on a boiling water-bath for 30-40 min. with passing argon through the solution which affected a complete transfer of ammonia into the HCl trap. The excess of HCl was determined by titration with standard 0.01−NaOH.

The studied substance $K_3Mn(CN)_5NO$ was prepared according to the method described in literature.[2] The identity of the substance was checked by IR spectra using the instrument UR 10, Zeiss Jena.

All other chemicals were of *pro analysi* purity grade (Lachema).

Results and Discussion

The Over-all Reduction Character. The complex anion $Mn(CN)_5NO^{3-}$ does not show any reduction

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(*) Part VI: *Inorg. Chim. Acta, 2,* 443 (1968).

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or oxidation at the mercury dropping electrode in the attainable potential range when using common supporting electrolytes, such as KCl, NaOH, Britton-Robinson buffers, or tetraalkylammonium salts. Only in presence of Cs^+ ions a reduction wave is observed coinciding at lower Cs^+ concentrations (0.2—0.4 *M*) with the reduction current of the supporting electrolyte. With increasing Cs^+ concentration the half-wave potential is shifted to more positive values (cf. Table I) and in 1 *M*—Cs^+ it is well developed and separated from the reduction current of the supporting electrolyte.

Table I. $E_{1/2}$ of the $Mn(CN)_5NO^{3-}$ Reduction Wave in Dependence on Cs^+ Concentration

CsCl Conc. (mole/l)	0.4	0.6	0.8	1.0	1.2
$E_{1/2}$(v.) *vs.* NCE	−1.775	−1.745	−1.735	−1.725	−1.715

Supporting electrolyte: 0.2 *M* NaOH

The observed phenomenon that the reduction of the complex anion is made possible by the presence of Cs^+ ions may be due to several factors. First of all it is necessary to consider the role of the ψ-potential which is strongly influenced by the presence of the polarizable Cs^+ ions and which lowers the enerby barrier of the reduction of highly negatively charged complex anions at the negative interface of the electrode. However, with respect to the fact that in absence of Cs^+ ions no depolarization is observed up to about −2.6 V which is the attainable potential in tetraalkylammonium salts, the facilitating influence of the Cs^+ ions amounts to more than 800 mV. It is evident that such a big shift of the half-wave potential cannot be due solely to the change of the ψ-potential and thus still other factors must be operative. The outer-sphere complex formation with the Cs^+ ions affecting considerable decrease of the effective charge of the complex particle, and the bridge mechanism of the electron transfer by formation of the activated bridge complex electrode-Cs^+-depolarizer are two other factors which can contribute to the mentioned shift. Both these processes are expected to occur preferentially with easily polarizable Cs^+ ions which explains the contrast to K^+ and Na^+ where no depolarization was observed up to 2 *M* concentration.

The height of the reduction wave is strongly dependent on pH of the medium. The corresponding dependence is shown in Figure 1 when the unit on the ordinate axis corresponds to the height of the first one-electron nitroprusside wave[6-8] at the given concentration. From this Figure it is seen that the limiting current attains the apparent value of about 3 electrons at pH > 12.5 whereas with decreasing pH the wave-height is increased up to pH > 8.5 where the limiting current coincides with the current of the supporting electrolyte.

The dependence of the wave-height on the complex concentration at various pH values of the medium is shown in Figure 2. In the region of pH > 12 and the concentration range from 4×10^{-4} to 4×10^{-3} *M* the concentration dependence is linear. With pH < 12 the concentration dependence deviates from linearity at concentrations above 1×10^{-3} *M*. This is due presumably to precipitate formation of $Mn(OH)_2$ (see further below) at the electrode surface which hinders the access of the depolarizer towards the electrode.

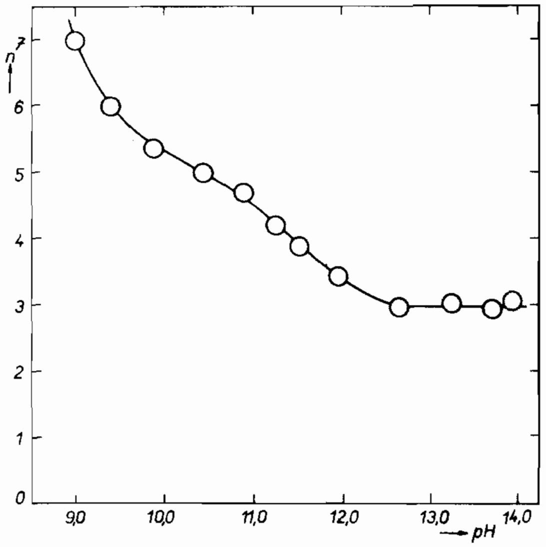

Figure 1. Limiting Current of the $Mn(CN)_5NO^{3-}$ Wave in Dependence on pH 1×10^{-3} *M* $K_3Mn(CN)_5NO$; 1 *M* CsCl, 0.8 *M* Britton-Robinson buffer; in pH region above 13 the alkality adjusted by NaOH.

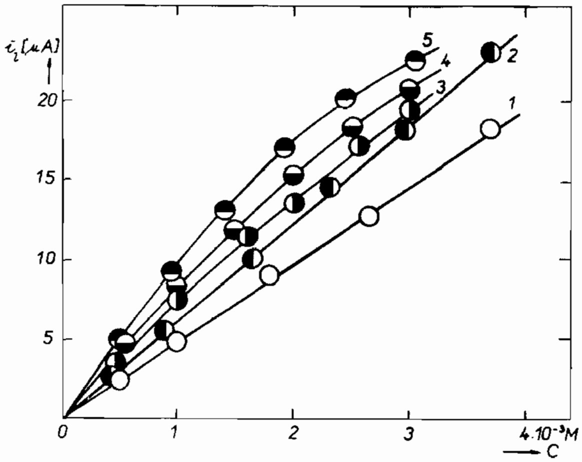

Figure 2. Concentration Dependence of the $Mn(CN)_5NO^{3-}$ Wave Height at Various pH Values of the Medium 1 *M* CsCl; 0.08 *M* Britton-Robinson buffer; pH: 1 12.6 (NaOH); 2 11.6; 3 11.0; 4 10.5; 5 9.4.

The reversibility of the electrode process was investigated using the Kalousek commutator method.[9,10] Experiments performed in the temperature range

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from 0° to 25°C proved a completely irreversible character of the electrode process; there was also no sign of active intermediates being inactivated with time which could possibly simulate the irreversibility.

The same conclusion was arrived at from the slow cyclic voltammetry experiments in which the hanging drop electrode was polarized with a potential sweep of 100 mV/s from positive to negative potentials and after reaching the deposition of the supporting electrolyte the polarization sweep was reversed. The voltammetric curves contained a well developed cathodic peak corresponding to the reduction of the complex but no anodic peak corresponding to a re-oxidation of the product. Also the oscillopolarographic $dE/dt-f(E)$ curves showed a distinct cathodic incision but no anodic one.

The results of the mentioned methods regarding the irreversibility of the electrode process were confirmed by the logarithmic analysis of the wave. The plot $\log(i/i_d-i))$ against E was linear and its slope $S = \partial E/\partial(i/i_d-i)$ had a value 105 mV which corresponds to a totally irreversible process. This value was obtained at pH 12.5 where the wave height corresponds to the uptake of 3 electrons showing that the apparent transfer coefficient α is rather low (approximately 0.2). A similarly low transfer coefficient was observed also in case of the third nitroprusside wave.[7,8]

Electrode Reduction Products. Products of the $Mn(CN)_5NO^{3-}$ electrode reduction were followed both using a microcell with the mercury dropping electrode as a working cathode, and a cell in which bottom mercury served as large area working cathode. Both methods yielded qualitatively concordant results. It was found that the reduction is accompanied by setting free the CN^- ions. From quantitative polarographic analysis of products of the exhaustive electrolysis it was established that all five cyanide ions are set free. During the electrolysis a dispersed white precipitare was formed which was identified after separation as $Mn(OH)_2$.

In the electrolyzed solution presence of ammonia was detected by means of the Nessler reagent. For quantitative determination of ammonia formed the solutions of various pH were electrolyzed under potentiostatic control and at the end of the electrolysis the ammonia was distilled off and determined in the way described in the experimental Section. The amount of ammonia calculated as percentage of the total amount of NO reduced to NH_3 was 49.6, 92.8 and 99.2% at pH 13.2, 9.85 and 9.05, respectively (each value is an average of four measurements).

During the reduction of the substance at the mercury dropping electrode evolution of small gas bubles was observed at the electrode surface. The gas evolution was most intense at $pH > 12.5$. In this pH region it is not likely that hydrogen evolution is involved and thus, also with respect to other observations, the most probable explanation is evolution of N_2 the bubbles of which are readily formed since the solution is saturated with nitrogen.

Limiting Current Character. From the dependence of the limiting current on pH of the medium it is evident that the over-all reduction mechanism of $Mn(CN)_5NO^{3-}$ involves chemical reactions which affect both the height of the limiting current and the composition of the products. This was confirmed by the dependence of the limiting current on the height of the mercury column from which it follows that the limiting current has not generally a diffusion character. The corresponding dependences for several selected pH values are plotted in Figure 3. It is seen that the plot $i_l-\sqrt{h}$ in most cases interesects the i_l-axis which is an indication of the semikinetic character of the current. The kinetic contribution observed in the pH region 12.5-14.0 is gradually diminished at lower pH values till at pH about 10.5 the dependence nearly corresponds to the diffusion-controlled process. With a further decrease of pH kinetic contribution increase again.

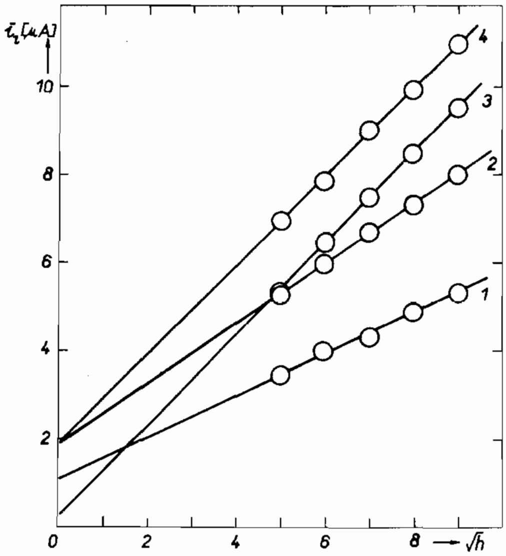


Figure 3. Dependence of the Limiting Current of $Mn(CN)_5NO^{3-}$ Wave on the Height of the Mercury Column 1×10^{-3} *M* $K_3Mn(CN)_5NO$; 1 *M* CsCl; 0.8 *M* Britton-Robinson buffer; pH: 1 12.6 (NaOH); 2 11.0; 3 10.5; 4 9.4.

Table II. γ-Values in Dependence on pH of the Medium

pH	13.80	12.60	11.40	10.80	10.50	10.10	9.40
γ	0.32	0.33	0.30	0.25	0.24	0.27	0.34

The character of the limiting current was checked also by the logarithmic analysis of the dependence of the instantaneous limiting current on time which is supposed to be given in the first approximation by the relation $i_l = \text{constant } t^\gamma$ (i_l is the instantaneous limiting current, t is the time elapsed from the beginning of the drop). In Table II the values of the coefficient γ are given for various pH of the medium. As seen, the γ-values are in the entire pH range studied higher than corresponds to diffusion controlled process (approximately 0.20) but considerably lower than those corresponding to purely kinetic processes. At the same time these results confirm conclusions obtained on basis of the dependence of the mean limiting currents on the height of the mercury column. At pH round 10.5 the γ-value approaches that expected for the diffusion-controlled process whereas both with increasing and decreasing pH the γ-value increases indicating an increasing kinetic character of the limiting current.

Influence of Cyanide Ions. In order to check the possible presence of intermediates containing substitution labile nitrosyl group the influence of cyanide ions on the reduction wave was studied. Since the addition of larger amounts of KCN is combined with considerable increase of viscosity of the medium and a corresponding lowering of the diffusion coefficient, parallel experiments were performed with $K_3Cr(CN)_6$. This compound possessing a similar structure and the same charge of the anion is supposed to be influenced by the viscosity effect in a comparable way as the studied complex. The results are shown in Figure 4. Curve *a* shows the experimental dependence for $Mn(CN)_5NO^{3-}$ and curve *b* corresponding to $Cr(CN)_6^{3-}$ represents the decrease of the limiting due solely to the change of the diffusion coefficient. Curve *c* was obtained from the curve *a* in which alowance was made for the diffusion coefficient change which is expressed by the curve *b*. It is seen that addition of CN^-—ions (pH 12.6) causes a rather steep decrease of the limiting current to a constant value corresponding to the uptake of 2 electrons. At this cyanide concentration the limiting current is strictly diffusion controlled as was shown from the analysis of i—t curves and dependence of the wave-height on the height of the mercury column.

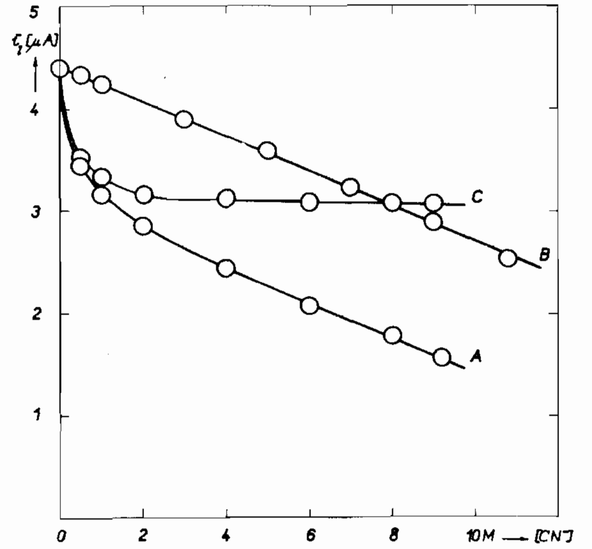
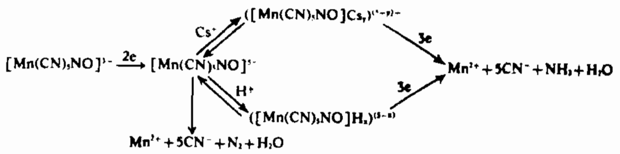


Figure 4. Influence of Cyanide Ions on Limiting Current of $Mn(CN)_5NO^{3-}$ and $Cr(CN)_5^{3-}$ Reduction Wave A: 1× 10^{-3} *M* $K_3Mn(CN)_5NO$; 0.2 *M* NaOH; B: 3×10^{-3} *M* $K_3Cr(CN)_6$ in KCN; C: graphical subtraction A-B.

From these results the following conclusions can be drawn. At pH 12.5 where the wave-height corresponds to the uptake of 3 electrons the primary 2-electron reduction is followed in absence of cyanide ions by a chemical reaction yielding another electroactive substance which is further reduced at the same potential. The product of the primary 2-electron reduction contains a substitution labile nitrosyl group which in presence of CN^-—ions is substituted yielding as a primary product the hexacyanide ion which cannot be further reduced.

Mechanism of $Mn(CN)_5NO^{3-}$ Reduction. The described experimental results are consistent with the following reaction mechanism:



According to this ECE reaction scheme the product of the primary 2-electron reduction can undergo 3 different competitive chemical reactions. One of them is the decomposition of the product to CN^-—ions, Mn^{2+} [precipitate $Mn(OH)_2$] and N_2 (gas bubbles at the electrode surface). Reaction competing with this one at high pH values where the limiting current is pH independent and corresponds formally to the uptake of 3 electrons is the outer-sphere complex formation with Cs^+ ions. The outer-sphere complex possessing a lower negative charge and containing the polarizable Cs^+ ion which can potentially function as a bridge can be reduced with the uptake of further 3 electrons to a product which is eventually decomposed to Mn^{2+} (formation of $Mn(OH)_2$ precipitate), CN^- ions (presence of 5 CN^- for one particle of the original complex found polarographically) and NH_3 (found as a product). From the results of electrolysis at the large-area electrode it follows that at pH 13.2 nearly 50% of analytical concentration of the original NO group is reduced to ammonia. The height of the wave should formally correspond according to the reduction scheme to about 3.5 electrons. A somewhat lower value observed at this pH (about 3 electrons) is presumably due to different conditions of electrolysis under which both quantities were obtained (polarography using mercury dropping electrode for determination of the number of electrons and large-area electrode electrolysis in stirred solutions for determination of the ammonia contents).

With decreasing pH the third reaction starts to operate, *viz.*, the protonation of the product of the primary 2-electron reduction. The protonated species undergoes a 3-electron reduction in a similar way as the outer-sphere complex yielding finally the same products Mn^{2+}, CN^-, and NH_3. With increasing protogenic strength of the medium the protonation rate inceases till in the pH range round 10.5 the total amount of the product of the 2-electron reduction is converted to protonated species and accordingly in this pH region a 5-electron diffusion-controlled wave is observed. In view of the fact that the protonation occurs in form of a rapid reaction preceding the electron transfer reaction the pK_{A1} value must be considerably lower than is the pH value at which the mentioned effects of protonation are polarographically observed. However, due to the higher negative charge of the complex $Mn(CN)_5NO^{5-}$ and to the electron rearrangement as compared with $Mn(CN_5NO^{3-}$ a much higher nucleophility in the former complex must be expected than in the latter. The pK_{A1} value for $Mn(CN)_5NO^{5-}$ can be roughly estimated to lie between 7 and 9.

The further continuous increase of the limiting current and its growing kinetic character with decreasing pH is unambiguously due to hydrogen evolution catalyzed be active intermediates. of the reduction, even if no detailed mechanism of this catalytic reaction can be given at present.

The reaction scheme is also substantiated by the described influence of CN^-—ions on the height of the limiting current. The substitution reaction with cyanide ions competes with and at high CN^- concentration considerably exceeds the rate of the outer-sphere complex formation or protonation thus hindering formation of species which can be further reduced. As a result the limiting current decreases in presence of higher CN^- concentration to the 2-electron, diffusion-controlled value.

When comparing the reduction of $Mn(CN)_5NO^{3-}$ with that of the isoelectronic nitroprusside ion[7,8] a remarkable analogy with the third nitroprusside wave is observed. In both cases the half-wave potential of the wave is strongly dependent on the nature of cations of the supporting electrolyte in a way which seems to be specific for the particular kind of the electrode process and which cannot be accounted for by the sole influence of the ψ-potential. The electrode reaction proceeds in both cases by the ECE mechanism (a chemical reaction interposed between two electron transfer reactions) involving as side reaction the inactivation of the product of the primary 2-electron reduction. The absence of the two single-electron waves[7,8] in case of $Mn(CN)_5NO^{3-}$ follows from extrapolation of the reaction pattern of the free NO^+ group and the nitroprusside ion to the manganese complex. The decrease of the N—O stretching frequency 2275 cm^{-1} (NO^+) to 1939 cm^{-1} (nitroprusside) is accompanied by the shift of the half-wave potential of the first single-electron wave by about 1.5 V towards negative values.[7,8,11,12] If the N—O stretching frequency can be considered as a semiquantitative measure of the metal $\xrightarrow{\pi}$ NO back donation combined with the corresponding decrease of the electron affinity in the redox orbital then in case of $Mn(CN)_5NO^{3-}$ ($\nu_{NO} = 1725$ cm^{-1}) the first single-electron wave which is dependent on the presence of the first wave cannot be observed. On the other hand the third wave in which the electrode proceeds by a completely different mechanism is not influenced to such a great extent by the electronic structure of the nitrosyl group in the original substance and hence in case of the manganese complex it becomes more positive than processes proceeding in two single-electron waves in case of the free NO^+ group and the nitroprusside ion.

The correlation between the electrophilic reactivity and the electronic structure of the studied complex is described elsewhere.[13]

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