

INTERMEDIATES OF ELECTRODE REACTIONS OF COORDINATION COMPOUNDS

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The redox properties of coordination compounds, *i.e.* their oxidation–reduction ability (given by the standard equilibrium potential), their oxidation–reduction reactivity (given by the rate with which they are able to react with various substances) and finally the mechanism of the particular reaction (given by the nature of the intermediates and products) represent a very important group of chemical properties of coordination compounds, closely related to their atomic composition and especially to their electronic structure. The redox properties of coordination compounds of transition metals have attracted a lot of interest since, unlike most organic and many inorganic compounds, they are able to undergo stepwise redox changes, passing through various more or less stable intermediates. The stability and configuration of these intermediates reflect the changes induced in the electronic configuration of the particle by the change of the number of electrons in the course of the redox process.

There are two main ways of studying the redox properties:

(1) The redox change in a compound is induced by the addition of some other substance, the redox agent, and the properties—kinetic or thermodynamic—of the system are studied by various physico-chemical methods. In this case the reaction with the electron donating or accepting agent proceeds in the whole volume of the solution, *i.e.* a homogeneous redox reaction is actually being followed.

(2) The redox change is induced by an inert polarized electrode which is able to donate or accept the electrons from the components of the solution. In this case the redox reaction proceeds at the boundary between the metal and solution only, so that a heterogeneous redox process is actually followed.

If the specific properties of a heterogeneous process are omitted for the present, a polarized electrode can be regarded as a redox agent and the homogeneous and electrolytic redox processes can be correlated on the same basis. In fact, there are very striking parallels between the rates and mechanisms of homogeneous and electrolytic redox reactions¹.

An electrode as the redox agent has, however, some specific properties in which it differs from the “homogeneous” redox agents and which must be taken into consideration when an homogeneous and an electrolytic process are compared. First of all it can be supposed, and all the experiments seem to confirm it, that there is almost no activation energy connected with the transport of the electron to or from the electrode; so far purely electrostatic effects connected with the potential drop at the interface are not considered.

This means that the rate and mechanism of the redox process, taking place at a certain potential, depends solely upon the structure and properties of the particles reacting with the electrode.

Secondly, the redox ability of a polarized electrode depends upon the potential impressed to it from an outer source. This means that the redox "strength" of an electrode can be varied in rather broad range, and that the process taking place at the electrode is in most cases the minimal redox change possible for the given compound. As an example let us compare the reduction of the dipyriddy(dipy) complex $\text{Mn}(\text{dipy})_3^{2+}$, at the dropping mercury electrode² and by various reducing agents in non-aqueous solvents (for summary see Herzog³): at the dropping mercury electrode a reduction to $\text{Mn}(\text{dipy})_3^+$ can be seen quite clearly at -1.5 V using 1 M lithium chloride in ethanol as solvent. This reduction is followed by the reduction of dipyriddy which starts at about -1.6 V. The homogeneous reduction has resulted in the formation of the 0 or -1 formal state of manganese only. This is due to the fact that there is no homogeneous reducing agent available, the strength of which would be exactly that needed for the formation of the $+1$ state. However, as the polarographic behaviour shows, the $\text{Mn}(\text{dipy})_3^+$ complex is quite stable and might be prepared, *e.g.* by controlled preparative electrolysis.

The third, and most important specific feature of an electrode is connected with the heterogeneous nature of its action: the redox process at the electrode is manifested by the charge transfer across the electrode-solution boundary. The current measured at a given potential depends upon the number of electrons which cross this boundary in a unit of time: if this rate is low, no electrode process is detected even if the redox ability of the electrode is sufficient from the thermodynamic point of view. The redox process then takes place, if at all, at a more negative (or positive) potential at which its rate increases to such an extent that the number of electrons transferred in a unit of time is considerable. [This statement is rather oversimplified. Actually, the measure of the extent to which the electrode reaction proceeds at a given potential is given by the ratio of the actual current to the hypothetical current which would flow through the electrode at the given potential for an infinitely rapid electrode reaction. If this ratio is small, the electrode reaction proper is slow and the potential of the process (expressed mostly as the half-wave potential) is more negative (or positive for oxidations) than the corresponding standard equilibrium potential of the system.] In homogeneous reactions, on the other hand, when sufficient time is given to the reaction mixture, most processes take place in accordance with thermodynamic requirements. This difference between the homogeneous and electrolytic reactions might result in great differences in the mechanism of these two types of processes. As an example the reduction of VO^{2+} can be quoted: under homogeneous conditions it is possible to reduce VO^{2+} to V(III) quite easily. At the dropping mercury electrode, on the other hand, the reduction of VO^{2+} proceeds very slowly at the potential corresponding to the $\text{VO}^{2+} \rightarrow \text{V(III)}$ standard potential; it takes place mainly at potentials which are more negative than that of the $\text{V(III)} \rightarrow \text{V(II)}$ reduction so that divalent vanadium is the product of the VO^{2+} reduction at the electrode. However if the redox inertness of VO^{2+} is removed (by increasing the

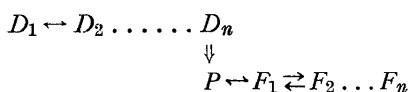
acidity of the solution in the presence of some anionic complexing agents, *e.g.* Cl^- ions⁴) the courses of the homogeneous and the electrolytic reductions are identical⁴.

So far only the so-called direct electrode reaction has been considered, *i.e.* a reaction which involves merely a change in the number of electrons in the particle, and no simultaneous change in the atomic configuration. Such a reaction proceeds at electrodes with a short time of electrolysis (as when using a dropping or streaming mercury electrode) only if a potential can be reached at which the rate of the process is sufficiently high. At large electrodes with prolonged electrolysis, such a reaction takes place with a very low current efficiency.

Most of the redox processes are, however, not direct electrode reactions but consist of a series of chemical reactions, preceding or following the electrode reaction proper. If a direct electrode reaction of D (depolarizer) giving P (primary product) is symbolized as:



a general electrode process might then be represented by a scheme:



where $D_1, D_2 \dots D_n$ are various species interconverted by chemical changes, but without any redox change. D_n is the species with the greatest redox reactivity, *i.e.* a species which at the given potential reacts with the greatest rate at the electrode. $F_1, F_2 \dots F_n$ are various final products of the electrode process, interconverted by chemical changes which might include homogeneous redox changes such as disproportionation or redox reactions with some component of the solution.

What has been said for the direct electrode reaction holds also for all these chemical changes: "*A chemical reaction can influence the electrode process only if its rate is sufficiently high*". At a dropping mercury electrode the lowest limit for the monomolecular reaction is at $k = 10^1$ to 10^2 l. mol⁻¹ sec⁻¹. If a reaction has a lower monomolecular rate constant it does not influence the mechanism of the electrode process at all. From this it follows that an electrode reaction might proceed along a different path from that of a homogeneous redox process. This is true especially for the interconversions of the products and intermediates: if these reactions are slow the electrode process (at least when studied by means of electrochemical methods) either stops at a product which is not thermodynamically the most stable one, or, at least the reaction of this product becomes the rate determining step and can be detected by the analysis of the experimental data. If it is remembered that a reaction is regarded from this point of view as "slow", even if it proceeds with a rate constant of the order 10^3 or 10^4 l. mol⁻¹ sec⁻¹, it can easily be seen that

many unstable intermediates, mostly those which are inaccessible by homogeneous methods, can be detected as products of electrode processes.

From many examples which might be quoted, the reduction of $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{dipy})_3^{2+}$ demonstrate this situation best (see *Figure 1*): homogeneous reduction of $\text{Ni}(\text{CN})_4^{2-}$ in aqueous solution results in all cases in the formation of $\text{Ni}_2(\text{CN})_6^{4-}$. In liquid ammonia, however, the reduction with solutions of alkali metals gives the zero-valent complex, $\text{Ni}(\text{CN})_4^{4-}$. The study of the electrode process shows⁵ (see *Figure 1*) that even in aqueous

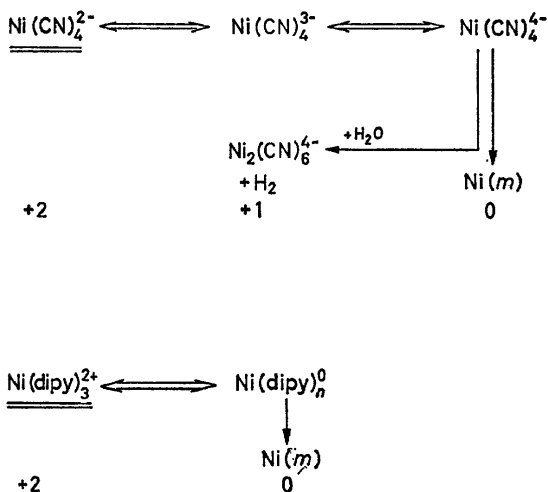


Figure 1. Simplified mechanisms for the reduction of $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{dipy})_3^{2+}$

solution the zero-valent complex is formed as the primary product, but is converted very rapidly into $\text{Ni}_2(\text{CN})_6^{4-}$ by reaction with water.

$\text{Ni}(\text{dipy})_3^{2+}$ is reduced at the electrode to the complex of zero-valent nickel, which rapidly decomposes to metallic nickel⁶. Homogeneous

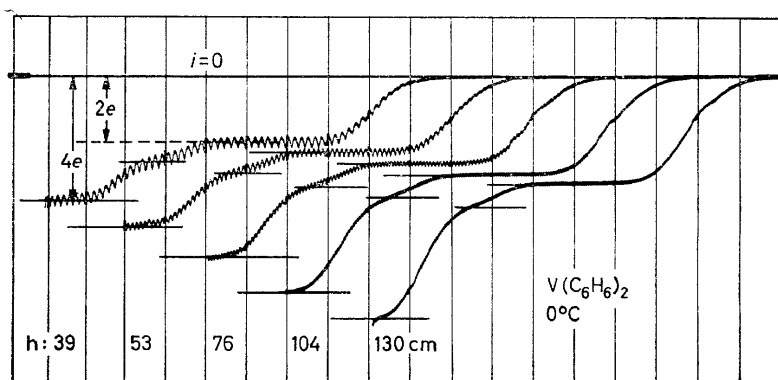


Figure 2. Oxidation of $\text{V}(\text{C}_6\text{H}_6)_2$ at a dropping mercury electrode (dependence upon the height of mercury reservoir). Solution: 1 M LiClO_4 in ethanol-benzene mixture (3:1), 1.5×10^{-3} M $\text{V}(\text{C}_6\text{H}_6)_2$; curves start at +0.4 V (aqueous 4 M NaCl calomel electrode); 100 mV/absc.

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reduction in aqueous or alcoholic solutions results in all cases in the formation of metallic nickel only.

The oxidation of V (benzene)₂ and V (diphenyl)₂ complexes represents examples of complicated reactions of intermediates⁷. Both complexes mentioned give three waves, the sum of which corresponds to a four electron oxidation of the vanadium. In fact, VO²⁺ is detected as the main final product. At low temperatures the first wave corresponds to a two electron oxidation (see *Figure 2*). At high temperatures the height of the wave increases above the value for two electrons, which shows that the product of the two electron oxidation undergoes a redox process, part of vanadium being oxidized to a higher state than +2. The complex formed by the two electron oxidation undergoes some further chemical change—its nature is not known as yet—in which a new species in the same oxidation state (+3) is formed and which is more easily oxidized than the primary product. The analysis of the polarographic behaviour leads to a scheme for the mechanism of oxidation which is summarized in *Figure 3*. The reactions of

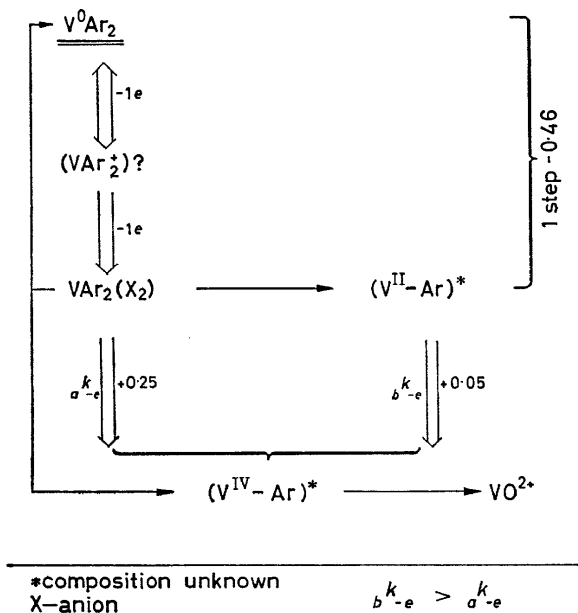


Figure 3. Oxidation mechanism of V(benzene)₂ in ethanol-benzene mixtures (preliminary)

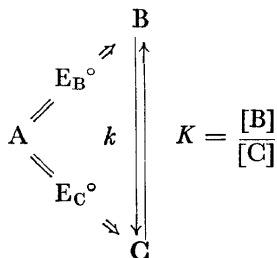
the divalent species are rather slow (the disproportionation reaction is actually at the detectable limit).

An even more complicated mechanism, involving various intermediates and products which are rapidly interconverted, has been found for the reduction of [Co(CN)₅X]³⁻ complexes^{8, 9}. These complexes give a series of waves (see *Figure 4*), the most positive one corresponding always to a one electron reduction to give the divalent cobalt complex. The behaviour of this divalent species does not depend upon the nature of X (when X = Cl⁻,

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can be assumed to be identical with the complex $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ which is supposed to be formed by reduction of Co(II)-cyanide complexes with borohydride or hydrogen¹⁰. *Figure 5* shows the simplified scheme of the reduction of $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ complexes. (The full scheme involves some other intermediates in the +2 state and the oxidation of the $\text{Co}(\text{CN})_5^{3-}$ complex.) Using this scheme, and the properties of various species detected and studied polarographically, it is possible to explain most of the reactions of Co(II)-cyanide complexes.

Many redox reactions can be supposed to proceed via a very active intermediate which is being inactivated in a reaction following the redox reaction proper. Let us consider the following system:



the properties of which are: $(-E_B^\circ) > (-E_C^\circ)$, $K < 1$; $bk_e \gg ck_e$. B and C are either various electronic isomers, or differ in atomic composition, etc. For such a system the equation holds: $-E_C^\circ = -E_B^\circ - (RT/nF) \ln K$.

In homogeneous reaction this system always reacts as a system with standard potential equal to E_C° , *i.e.* A can be reduced even with redox agents having lower standard potentials than E_B° . At the electrode, however, the reduction will proceed via B (due to the difference in rate constants of the two possible reduction paths), and the total behaviour will depend upon the rate of the interconversion of B into C. If k is small, the process $A \rightarrow B$ can be followed directly.

Such a behaviour, complicated however by other reactions, has been observed where A is $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$. This ion shows a one electron reduction at -1.18 (this reduction was first observed by Griffith, Lewis and Wilkinson¹¹). However, as the pH of the solution decreases, the height of the wave increases above the value for one electron, reaching the value for a two electron reduction at $\text{pH} \approx 2$ ¹². At the same time, the half wave potential shifts to more positive potentials (*see Figure 6*). In acidic solutions a second three electron wave is obtained at more negative potentials. The reduction mechanism of the whole system is shown on *Figure 7*¹². As the most important feature of this mechanism, it must be emphasized that the species $[\text{Cr}(\text{CN})_5\text{NO}]^{4-}$, the primary product of the one electron reduction, is not reducible as long as it does not accept two protons. The polarographic behaviour shows that the primary product might be stable in solutions having low hydrogen ion concentration, and in fact we succeeded in preparing the compound $[\text{Cr}(\text{CN})_5\text{NO}]^{4-}$ by controlled electrolysis in 0.1 M sodium hydroxide solution (*Figure 8*). At $\text{pH} < 9.5$ no reduction product can be detected in the solution, decomposition taking place.

In the course of the study of the homogeneous reduction of $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ by $\text{Co}(\text{dipy})_3^{+1}$ it was, however, found that the univalent cobalt is easily oxidized by the chromium complex, in spite of the fact that the redox potential of the chromium couple is about 250 mV more negative than that of the $\text{Co}(\text{II})\text{--Co}(\text{I})$ dipyriddy couple. Another striking result was found

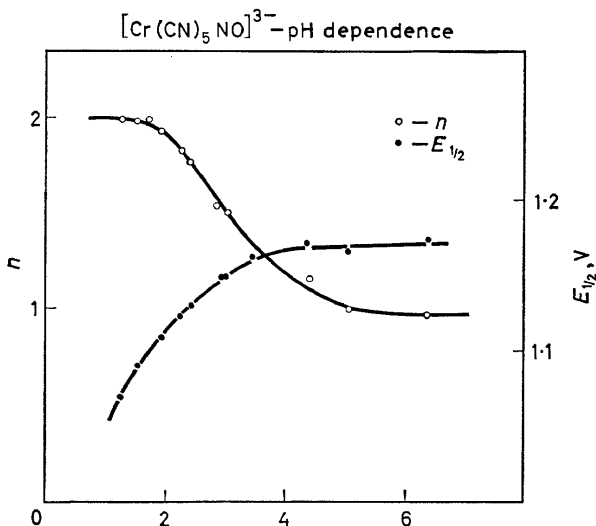


Figure 6. Dependence of the number of accepted electrons (n) and of the half-wave potential ($E_{1/2}$) upon pH for the reduction of $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$

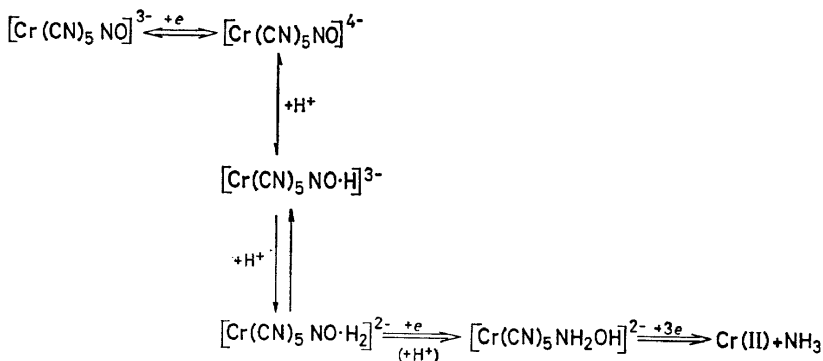
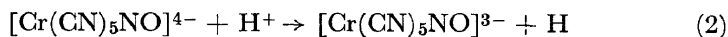
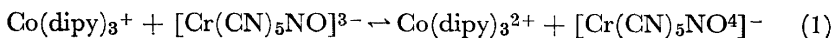


Figure 7. Mechanism for the reduction of $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$

when studying this reaction. The $\text{Co}(\text{I})$ complex is completely oxidized even by sub-stoichiometric amounts of the $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ compound (100:1!), and after the reaction the original amount of $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ can still be detected in the solution. This means that the chromium complex actually catalyses the oxidation of the $\text{Co}(\text{I})$ dipyriddy complex at the

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expense of hydrogen ions. The study of the mechanism of this process has shown that the reaction actually proceeds via the $[\text{Cr}(\text{CN})_5\text{NO}]^{4-}$ species according to a mechanism which (simplified and omitting intermediate steps) can be represented as:



The equilibrium (1) is strongly shifted to the left, but as the reduced chromium species is removed by protonization and subsequent re-oxidation,

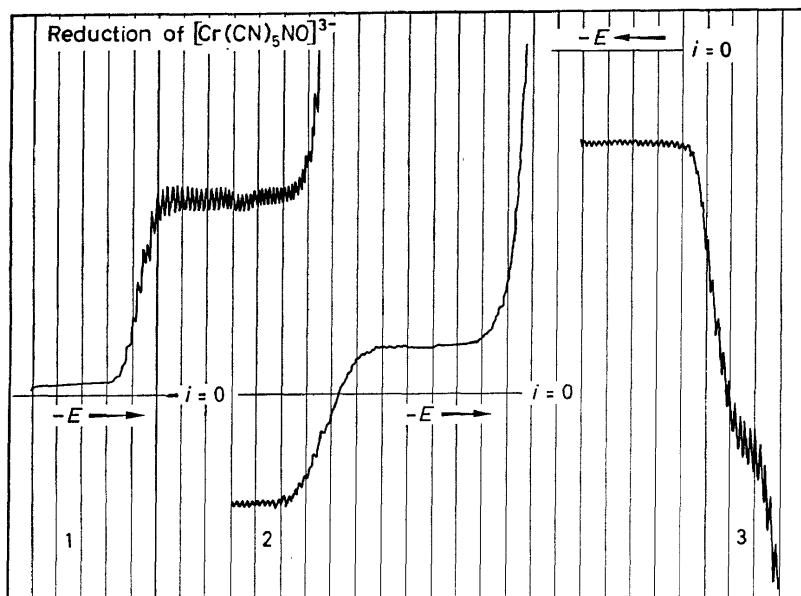


Figure 8. Electrolytic reduction of $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ in 0.1 M NaOH solutions; curve 1— 10^{-3} M $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$; curve 2—After 30 min of electrolysis at a mercury pool electrode, $E = 1.4$ V; curve 3— CN^- ions liberated by decomposition of the product

all the Co(I)-dipyridyl complex is consumed without any actual change in the concentration of $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$. The protonization of the $[\text{Cr}(\text{CN})_5\text{NO}]^{4-}$ species proceeds rather rapidly, but the intramolecular redox process which follows this protonization is relatively slow and is "cut off" from the electrode reaction which thus proceeds by a completely different path from that of the homogeneous redox reaction. However, when very strong reducing agents are used, the homogeneous reaction results in the same products as the electrode reaction¹².

The reduction of $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ thus represents a typical example of the general type of redox process discussed above and, to my knowledge, the only one known at present.

It would be possible to give many more examples of systems in which the

paths of electrolytic and homogeneous redox reactions differ. I hope, however, that the examples quoted here suffice to illustrate the most important ways in which electrode redox processes differ from homogeneous ones. As has been seen, when the specific properties of an electrode as a redox agent are taken into account, the differences between the two types of processes can be rationalized.

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