

ELECTROREDUCTION OF AROMATIC NITRO COMPOUNDS: CASE FOR COMPARISON OF INFORMATION OBTAINED BY POLAROGRAPHY AND VOLTAMMETRY

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Dedicated to Professor Václav Horák on the occasion of his 70th birthday.

The difference between the information obtained by d.c. polarography (which is virtually a potentiostatic method) and cyclic voltammetry (CV), where products formed at one potential can affect electrolysis at another potential is discussed. The principle is demonstrated on reduction of nitrobenzenes, where at DME the reduction usually occurs as a strictly four-electron process, whereas in CV the arylhydroxylamines formed react with an intermediate of the four-electron reduction.

It is sometimes assumed that polarography, which involves recording of current-voltage curves using a dropping mercury electrode (or another electrode with a periodically renewed surface, such as a streaming mercury electrode), yields information about a given electrode process which is identical with the information obtained by linear sweep or cyclic voltammetry, where the entire voltage scan is carried out using an electrode with an unchanged surface, such as a hanging drop of mercury, or a solid carbon, gold, or platinum electrodes.

Whereas in some cases the patterns of reactions – both chemical and electrochemical – obtained by both techniques may be identical, in others they are not. This is predominantly due to two factors – the difference in the duration of the time-window used for current measurements in the two techniques and the difference in surface conditions. In polarography the information obtained by the current measurement is averaged over the duration of the drop-time, usually 2 – 4 s. In voltammetry, where voltage scanning rates of the order of 10 mV s^{-1} to 10 V s^{-1} are typically used, the electrode is in contact with the surrounding solution at a given potential only for a fraction of a second. Consequently, slower chemical reactions which do not affect the peak currents in voltammetry can play a role and govern the intensity of limiting currents in polarography. The other factor which can result in a difference in information available from polarography and voltammetry results from the fact that polarography is – from

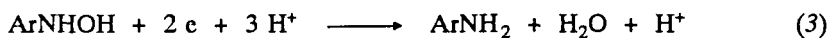
the point of view of electrolysis – in principle a potentiostatic method. During the life-time of each drop the potential namely remains practically constant and varies at commonly used scanning rates only by some 10 to 20 mV – a small change in the overall voltage span of 1 or 2 V. Moreover, products formed at one potential do not affect the electrolysis at another potential, as the drop at potential A is different from that grown at potential B. Furthermore, the rate of potential scanning in polarography does not affect the extent of reactions of electrolysis products, as the product on a drop formed at potential A does not remain in the vicinity of the electrode when the drop at potential B is formed.

On the other hand, in voltammetry the voltage applied to a given electrode varies with time and moreover, the products of electrolysis formed at one potential can affect electrode processes at another potential. In cyclic voltammetry the products formed by reduction can interact with products undergoing or formed by oxidation and vice versa. As the electrolysis products as well as products of consecutive reactions are transported from the electrode towards the bulk of the solution by diffusion, the rate of this transport competes with the rates of consecutive chemical reactions. As the time-span available both for a chemical reaction and the transport of diffusion plays a role in voltammetry, the extent of the consecutive reaction is in this technique a function of the rate of scanning. By choosing an appropriate rate of scanning it is possible to eliminate or enhance the effect of a consecutive chemical process.

The above evaluation of the situation in polarography and voltammetry does not make an attempt to prefer one or the other technique, but rather to stress that these two techniques may offer a different kind of information, both of them of some importance. They should be considered as complementary rather than competitive and to use just one of them often yields a less complete information.

An example of a system demonstrating the difference between the information obtained by polarography and voltammetry is the reduction of nitrobenzene in aqueous buffered solutions. Nitrobenzene was actually the first organic compound for which a polarographic current–voltage curve was reported¹ back in 1925. Since then a considerable volume of information has been gathered on polarographic reduction of nitrobenzene and many other aromatic nitro compounds^{2–4}. All this evidence indicates that for the majority of simple nitro compounds the reduction occurs in principle in two steps: A four-electron reduction of the nitro group to an arylhydroxylamine (1) followed in acidic media by a two-electron reduction of a protonated form of the arylhydroxylamine, resulting in a formation of an amino derivative (2), (3):





With the exception of some increase in strongly acidic media⁵ (attributed to a formation of some azoxybenzene and its successive reduction) for all nitro compounds (provided that they do not bear an acidic or a basic group as a substituent) a single four-electron wave was always observed over the entire pH-range studied (*o*- and *p*-nitrophenols and nitroanilines follow a different pattern). At concentrations of the nitro compound below about $5 \cdot 10^{-4} \text{ mol dm}^{-3}$, no deviations of the intensity of the limiting current from that expected for a four-electron diffusion controlled process were observed that would indicate a chemical reaction between the products and the parent compound or reduction intermediates.

Similarly, no information about the presence of competing reactions has been obtained from the height of the second, more negative wave of the corresponding arylhydroxylamine in acidic media⁶⁻⁸. Even when the measurement of the exact height of this wave may be difficult (due to the presence of several waves, autoinhibition phenomena and irreversibility of the cleavage of the N-O bond), this wave reaches in sufficiently acidic solutions a height corresponding to a two-electron diffusion controlled process.

Extension of polarographic studies is possible using a rectangular voltage polarization in the Kalousek commutator^{9,10}. In this method reduction products are formed during the first half of the pulse and their concentration measured in the second half. Using a dropping mercury electrode and a similar rate of voltage scanning as in classical polarography, current-voltage curves show the concentration of the oxidation product formed at a chosen potential. Our investigations indicated theoretical and pH-independent yield of arylhydroxylamine, corresponding to a two-electron diffusion controlled process.

Similarly, when electrolysis products are removed from the electrode surface by convection at a gold rotating disk electrode (under conditions when a four-electron reduction is preferred) a theoretical yield of phenylhydroxylamine was reported¹¹, when the anodic current of its oxidation was measured on a ring electrode.

From the shifts of polarographic half-wave potentials with pH it is possible to show¹² that the transfer of the first electron is preceded at pH smaller than about 10 by a protonation of the nitro group. From a decrease of the limiting current with increasing pH in the presence of 10 – 50% DMF (ref.¹³), it is possible to conclude¹² that another proton transfer occurs between the first and the second electron transfer.

The situation is, nevertheless, different when stationary electrodes – mercury or solid – are used. For voltammograms of a diffusion controlled process, in which a single species – i.e. nitrobenzene – is transported by diffusion to the electrode surface, the ratio of peak heights should be proportional to the ratio of the number of electrons transferred to the power of 3/2. Hence when the peak current of the four-electron reduction of the nitro group to a hydroxylamino group ($i_{\text{NO}_2}^{\text{e}}$) is compared with the peak

current corresponding to the two-electron oxidation of the hydroxylamino group yielding nitroso group ($i_{\text{NHOH}}^{\text{a}}$), their ratio should be approximately 2.83. Moreover for the reversible two electron process involving oxidation of the electrogenerated arylhydroxylamine ($i_{\text{NHOH}}^{\text{a}}$) and reduction of the corresponding nitroso compound (i_{NO}^{c}) a ratio of peak currents 1 : 1 would be expected. Such ratio $i_{\text{NHOH}}^{\text{a}} : i_{\text{NO}}^{\text{c}} = 1 : 1$ is actually found when nitrosobenzene or phenylhydroxylamine are introduced into the studied solution.

On the other hand, when nitrobenzene is added to the buffer used as supporting electrolyte, the resulting current-voltage curve shows¹⁴ at the moderate scanning rate used, the ratio $i_{\text{NO}_2}^{\text{c}} : i_{\text{NHOH}}^{\text{a}}$ significantly larger than 2.83 and the ratio $i_{\text{NHOH}}^{\text{a}} : i_{\text{NO}}^{\text{c}}$ greater than 1.0. With increasing rate of potential scanning the values for both these ratios decrease and limit to the theoretical value. At a given rate of voltage scanning the values of both ratios $i_{\text{NO}_2}^{\text{c}} : i_{\text{NHOH}}^{\text{a}}$ and $i_{\text{NHOH}}^{\text{a}} : i_{\text{NO}}^{\text{c}}$ are found practically independent of pH between pH 4 and 11 when a hanging mercury drop electrode is used.

In buffered solutions the ratios $i_{\text{NO}_2}^{\text{c}} : i_{\text{NHOH}}^{\text{a}}$ and $i_{\text{NHOH}}^{\text{a}} : i_{\text{NO}}^{\text{c}}$ are independent of concentration of nitrobenzene. When both nitrobenzene and nitrosobenzene are added in equimolar concentrations to a buffer, the heights of both peaks $i_{\text{NHOH}}^{\text{a}} : i_{\text{NO}}^{\text{c}}$ are additive.

When a solution of nitrobenzene was electrolyzed at HMDE at a potential, where the first four-electron reduction occurs and the anodic peak $i_{\text{NHOH}}^{\text{a}}$ is recorded at various times during electrolysis, the yields of phenylhydroxylamine were significantly smaller than would correspond to a complete conversion of nitrobenzene. Controlled potential electrolysis with a large mercury pool electrode and following the progress of electrolysis either electrochemically using anodic wave of phenylhydroxylamine or spectrophotometrically yielded similar results.

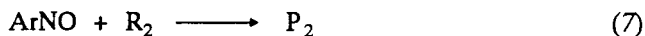
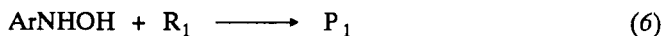
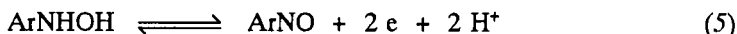
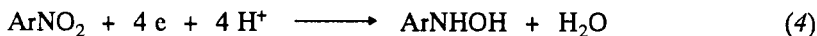
Cyclic voltammetric experiments as well as control potential electrolyses indicate hence presence of a chemical parent-child reaction resulting predominantly in a formation of an electroinactive species.

Among chemical reactions that can occur in the reaction mixture it is first possible to exclude reactions involving the parent nitro compound with final electrolysis products. Under reaction conditions used the nitrobenzene is namely stable in the presence of both nitrosobenzene and phenylhydroxylamine. Absence of a reaction between the parent nitro compound and the generated phenylhydroxylamine is also supported by the heights of dc polarographic limiting currents which correspond practically exactly to a four- and six-electron process. In a case of a parent-child reaction of this type deviations towards smaller total current would be expected.

Another reaction, the presence of which may be considered in solutions containing nitrosobenzene and phenylhydroxylamine, is formation of azoxybenzene and/or its precursor. This reaction can be excluded as predominant, because it is acid and base catalyzed and no azoxybenzene is rapidly formed in a homogeneous reaction above pH about 3 and below pH 11.5. If this reaction were the predominant pathway for deacti-

vation of ArNO and ArNHOH, both species would be removed from the reaction mixture by the same rate and the ratio $i_{\text{NHOH}}^a : i_{\text{NO}}^c$ would be close to 1.0. This ratio being considerably higher than one also rules out a formation of an electroinactive precursor of azoxybenzene, such as ArN(OH)N(OH)Ar as the main reaction path.

Available experimental evidence indicates sequence (4) – (7),



Independence of the ratios $i_{\text{NO}_2}^c : i_{\text{NHOH}}^a$ and $i_{\text{NHOH}}^a : i_{\text{NO}}^c$ of pH in the range between pH 4 and 11 indicates that rates of reactions (6) and (7) are practically pH-independent. Reagent R₁ may be either identical to R₂ or different, but neither of reagents involved is the solvent, as both ArNHOH and ArNO are stable under these conditions. The independence of pH indicates that reagents R_i are neither hydrogen nor hydroxide ion. Absence of this reaction under quasi-potentiostatic conditions in dc polarography indicates that the reaction involves products (phenylhydroxylamine, nitrosobenzene) formed at one potential with intermediates of an electrode process occurring at different potential (in the reduction of the nitro group). The radical ArNO₂H^{*} is currently considered to be most probably the reagent R.

This example indicates the importance of using both polarography and voltammetry in the studies of mechanisms of organic electrode processes. Whereas polarography offers in the most straightforward way information about the overall process and in particular about reactions occurring before the first electron uptake, voltammetry yields useful information about consecutive processes and enables sometimes to detect unexpected reaction paths. Both informations could be useful in electrosynthetic studies.

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