SOME APPLICATIONS OF POLAROGRAPHY FOR INVESTIGATION OF EQULIBRIA IN AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th anniversary of the Nobel Prize for polarography.

There are two possibilities how to follow equilibria of organic compounds established in aqueous solutions using polarography: for very fast reactions, information can be obtained from shifts of half-wave potentials. For slowly established equilibria, the changes in the limiting current are followed. In both cases variation of the half-wave potentials or limiting currents with concentration of a reactant, present in excess, is followed. The types of reactions, which had been followed in this way, are as follows: hydration–dehydration equilibria, additions of hydroxide ion to carbonyl and nitroso compounds, the role of slowly established acid–base equilibria involving C-acids; further also reactions involving the addition of ammonia, primary amines, hydroxylamine, and hydrazine to carbonyl compounds.
Keywords: Electroreductions; Electrooxidations; Polarography; Electroactivity; Structure; Organics.

There are three main types of chemical equilibria, which can be followed by polarography. There are reactions, where the equilibria are established rapidly; in such cases a single polarographic wave is observed and shifts of half-wave potentials of these waves are followed.

To the second group belong reactions, where the rate of establishment of chemical equilibria is comparable with the rate of transport of electroactive species to the electrode. In such cases, we are able to observe kinetics of the chemical reaction yielding the electroactive species, but cannot always determine the equilibrium constant.

In the third group are equilibria that are established slowly, when compared with the rate of transport of electroactive species, usually diffusion. In such cases two waves are obtained on polarographic curves (Fig. 1). The

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ratio of these waves, as a function of concentration of the species present in excess in the solution, enables the determination of the equlibrium constant. This type of investigation of equilibria can be often compared with spectrophotometric measurements[1].

Before attempting to use either the potential shifts or changes in the limiting currets for investigation of equilibria, it is therefore essential to recognize the nature of the currents involved, particularly, if they are kinetic or diffusion-controlled.

NUCLEOPHILIC ADDITIONS

Addition of Water to Carbonyl Groups

For reductions of carbonyl compounds in aqueous solutions the addition of water (*1*) plays an important role, particularly when the activity of the C=O group is increased by substitutents in the vicinity, which exert inductive or

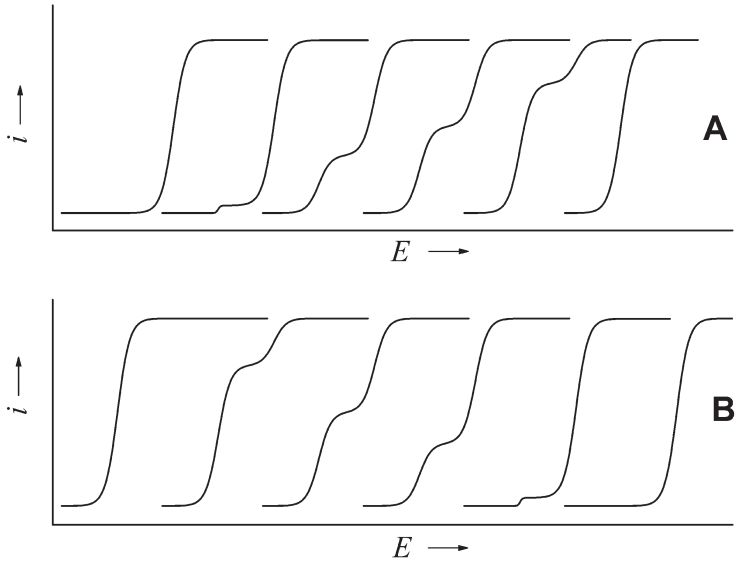


FIG. 1
Dependence of limiting currents on cencentration of the reagents. Concentration of the reagent in excess increases from left to right (A) Product of the reaction is reduced at more positive potentials than the parent compound (Example: Reaction of carbonyl compounds with primary amines). (B) Product of the reaction is reduced at more negative potentials than the parent compound (Example: Reaction of 1,2-diketones with water).

resonance effects. In these compounds values of equilibrium constants can be determined only over a pH range, where the rate of dehydration is neither acid- nor base-catalyzed.

$$>CH{=}O + H_2O \rightarrow >CH(OH)_2 \qquad (1)$$

Examples of such diffusion currents are those of chloral and bromal, which are present in aqueous solutions in more than 90% as hydrated forms. It is with these strongly hydrated aliphatic compounds that polarography can be used for determination of equilibrium constants.

When the formyl group is attached to the phenyl group in benzaldehyde, the degree of hydration is oppositely very small[1]. It is only with strongly negative substituents in positions 2 or 4 that considerable hydration occurs also in substituted benzaldehydes. Among those, orthophthalaldehyde is an example, where the diffusion current is observed only in a limited pH range, namely between pH 4 and 8 (Fig. 2).

Determination of the hydration–dehydration equilibrium constant is possible only over a pH range, where the limiting current is independent of pH. For example for orthophthalaldehyde such pH independent current is observed at pH 4–8 (Fig. 2). The current increasing at pH lower than this pH-independent region is catalyzed by acids. The currents at pH values higher than in this pH-independent region are catalyzed by a base. From these currents the information about the kinetics of the dehydration can be obtained, but not information about the position of the hydration–dehydration equilibria.

Among heterocyclic compounds, the pyridinecarboxaldehydes are strongly hydrated. The effect of the heterocyclic nitrogen is almost comparable with that of nitro group in coresponding position in benzaldehydes[2].

Considerable hydration has been also observed in 2-formylimidazole. On the other hand, five-membered heterocyclic compounds, such as furan or thiophene derivatives, are only very slightly hydrated.

Conjugation plays an important role in the hydration of 1,2-diketones[2–6] (*2*) and in compounds, where a C=O group is adjacent to a COOH, COO^- or COOR group[7–9]. In physical organic chemistry and in organic electrochemistry, there are numerous rules which have exceptions. One rule, from which this author does not know of any exception, is the fact that the conjugate acid is always more easily reduced. This means that a reduction of the acid form occurs at a more positive potential than that reduction of the corresponding base. On the other hand, the oxidation of a conjugate base

takes place always easier, at more negative potentials, than that at which the corresponding acid is oxidized.

$$O{=}C{-}C{=}O + H_2O \rightarrow O{=}C{-}C(OH)_2 \qquad (2)$$

ADDITION OF HYROXIDE IONS[10–25]

In reactions with organic compounds, hydroxide ions can function not only as a base, but also as a nucleophile, sometimes as both. As OH^- is a strong base, but not a very strong nucleophile, its nucleopholic additions are often observed at pH > 10.

Additions of OH^- to Aromatic Aldehydes

Most of benzaldehydes and five-membered aromatic aldehydes are in aqueous solutions less than 5% hydrated when OH^- ions are added to the formyl group (*3*) and to the resulting species. The geminal diol undergoes a two-electron electrooxidation to a carboxylic acid.

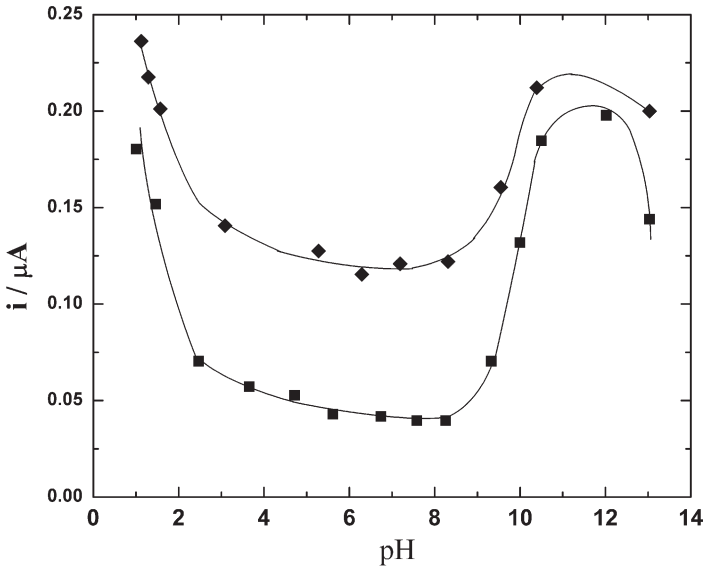


FIG. 2
Dependences of limiting currents of 0.1 mM orthophthalaldehyde on pH. Squares: in buffers containing 1% acetonitrile; diamonds: in buffers containing 30% acetonitrile.

$$ArCH{=}O + OH^- \rightarrow ArCH(OH)O^- \quad (3)$$

For strongly hydrated species, which are present in aqueous solutions predominantly in the geminal diol form, the behavior in alkaline solutions indicates, that the reaction with water or hydroxide ions results in dissociation of the geminal diol forming an oxidizable geminal diol anion (*4*). Both the addition of hydroxide ions to carbonyl groups or the dissociation of the geminal diol are very fast reactions, in which the geminal diol anion, that undergoes oxidation, is formed by reactions with rate constants highter than about 10^4 l mol^{-1} s^{-1}.

$$>CR(OH)_2 + OH^- \rightarrow >CR(OH)O^- \quad (4)$$

In physical organic chemistry and in organic electrochemistry, there are number of rules which have exceptions. One rule, from which this author does not know of any exception, is the fact that corresponding acid is always more easily reduced. This means that a reduction of the acid form occurs at more positive potentials than the reduction of the corresponding base. On the other hand, the oxidation of a corresponding base takes place always easier at more positive potentials, when corresponding acid is oxidized.

An example following this principle is the oxidation of benzaldehyde in alkaline solutions. In such solutions hydroxide ions are added to the formyl group with rate constants higher than about 10^4 l mol^{-1} s^{-1}. The oxidized species is the geminal diol anion. For strongly hydrated species which are present in aqueous solution predominantly in the geminal diol anion forms, the behavior in alkaline solutions indicates, that the reaction with water or hydroxide ion results in dissociation of the geminal diol forming a geminal diol anion (5).

$$ArCH(OH)_2 + OH^- \rightarrow ArCH(OH)O^- + H_2O \quad (5)$$

As these are examples of fast chemical reactions preceding the electron transfer, it is possible in some instances to determine the equilibrium constants from the shifts of the half-wave potentials. In strongly alkaline solutions at pH > pK_a, the same predominant species is present, that means the geminal diol anion is present in solution and the same species undergoes more easily electrooxidation. Therefore, the half-wave potencials in strongly alkaline solutions are pH-independent (*6*). With decreasing pH the activity of hydroxide ions decreases, and the half-wave potential of the anodic

wave of oxidation of the geminal diol anion is shifted to the more to positive values. The intercept of the twolinear segments (Fig. 3) of the $E_{1/2}$–pH plots coresponds to the pK_a value.

$$\mathrm{ArCH(OH)O^-} \rightarrow \mathrm{ArCOO^-} + 2\ \mathrm{e} + 2\ \mathrm{H^+} \qquad (6)$$

Additions of Hydroxide Ions to Nitrosobenzene

Reactions of nitroso compounds with various nucleophiles have been reported[26], but only reactions between nitrosobenzene and hydroxide ions have received some attention based on electrochemical data[27]. In strongly alkaline solutions a single wave is observed, which is anodic, corresponding to the oxidation of the geminal diol anion formed by addition of hydroxide ions to nitroso group (*7*). In strongly alkaline solutions the half-wave potential of this wave remains pH-independent.

$$\mathrm{ArNO} + \mathrm{OH^-} \rightarrow \mathrm{ArN(OH)O} \qquad (7)$$

A decreased activity of hydroxide ions results in a shift of the potentials to more positive values. In such solutions the geminal diol anion formed from the nitroso group predominates. With decreasing pH the activity of hydroxide ions decreases, and the anodic wave decreases. In the $E_{1/2}$–pH plot there are two linear segments (Fig. 3). The pH, at which the half-wave potential of the anodic wave becomes pH dependent, corresponds to the pK_a value of the addition of the hydroxide ions to the nitroso group.

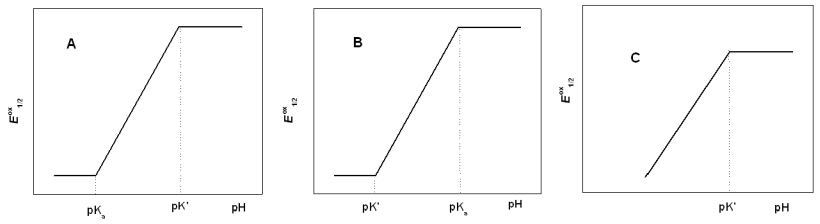


FIG. 3
Role of rapidly established antecedent acid-base equilibria on half-wave potentials: (A) conjugated acid is reduced; (B) conjugate base is oxidized; (C) data in strongly acidic media are not accessible.

Additions of Hydroxide Ions to Activated C=C Double Bonds[28,29]

In compounds carrying an α,β-unsaturated carbonyl grouping, the addition of hydroxide ions takes place to the carbon–carbon double bond (*8*). For most frequently investigated compounds, this reaction is followed by a rapid cleavage of the C–C bond resulting in the formation of an aldehyde and an aldol. A similar addition takes place to phenyl vinyl sulfone[30].

$$\mathrm{ArCOCH{=}CHAr' + OH^- + H^+ \rightarrow ArCOCH_2CH(OH)Ar'} \qquad (8)$$

ROLE OF PROTON TRANSFER

The reduction of an acid form takes always place at more positive potentials than that of the corresponding base. Consequently, if the surface protonation takes place sufficiently rapidly, it is the acid form, that is reduced, even at pH when it is the conjugate base, which predominates in the bulk of the solution. In the vicinity of the electrode the conjugate base must be converted into the more easily reduced acid by protonation. As long as the protonation is fast enough, a single wave is observed, the half-wave potential of which is shifted to more negative potentials with increasing pH. This is due to the fact that with increasing pH more energy is needed to convert the conjugate base into the corresponding acid. If a sufficiently low pH is reached, which corresponds to the pK_a of the reduced acid, the half-wave potential becomes pH-independent (Fig. 3).

In the opposite direction, with increasing pH, the half-wave potential of the reduction of the protonated form is shifted to more negative potentials. The dependence of the half-wave potentials on pH is linear, until a pH range is reached, where the rate of protonation is not sufficiently fast to convert all of the base form, predominant in the bulk of the solution, into the conjugate acid. From the pH at the intersection of the two linear segments and known pK' value (from the i–f(pH) plot), it is possible in some cases to obtain the rate constant of the protonation reaction taking place at the electrode surface.

In many instances a sufficiently low pH value cannot be reached, where the half-wave potential becomes pH-independent because of low value of the pK_a. For example, the reduction of aromatic carbonyl compounds takes place in acidic media in a single one-electron step. This reduction corresponds to the transfer of the electron to the protonated form of the carbonyl compound [(*9*) and (*10*)]. The pK_a of protonation of compounds like benzaldehyde or acetophenone are in the range of –4 to –5. As the reduc-

tions are usually not followed to such high acidity, information about the pK_a value from polarographic data is often not accessible.

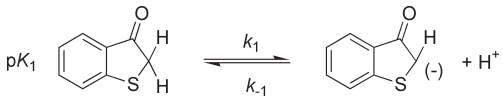
$$>C=O + H^+ \rightleftarrows [>C=OH]H^+ \quad (9)$$

$$[>C=OH]H^+ + e \rightarrow [C–OH]H \quad (10)$$

In numerous instances the limiting current of the conjugate acid decreases with increasing pH. This occurs over a pH range, where the protonation of the base form at the vicinity of the electrode is not fast enough to convert all the predominant conjugate base into the corresponding acid. The pH range, in which this decrease takes place, depends on the rate of protonation and on the pK_a of the acid. It does not offer simple information about the pK_a of the acid.

It is only in the cases, where the protonation rate is very slow, that polarography offers direct information about the pK_a of the acid–base reaction involved.

The majority of acid–base reactions involving O-, N-, and S-acids lead to a rapid establishment of the acid–base equilibria. It is only in the reduction of the C-acids, involving a cleavage of the C–H bond. The results in slowly established acid–base equilibria, that polarography can be used for determination of pK_a values. To achieve the dissociation of the C–H bond, the group, that undergoes dissociation, must be activated by neighboring groups. Most common examples of such acids are 1,3-diketones and other 1,3-dicarbonyl compounds[31–36] as well as compounds involving sulfur, such as 3-phenacylthianaphhenone[37] (*11*), phenacyl sulfides and phenacyl sulfonium compounds[38].



(*11*)

ADDITION OF AMMONIA, PRIMARY AMINES, OR AMINO ACIDS TO CARBONYL COMPOUNDS

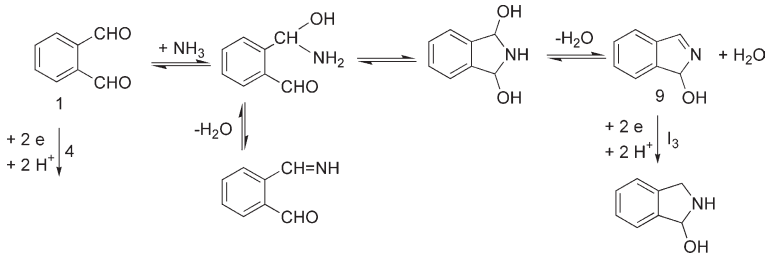
Primary amines add to carbonyl compounds to yield a hemiaminal (carbinolamine) (*12*), which is in most cases rapidly converted by its dehydration. This imine is in most cases reduced at more positive potentials than the starting carbonyl compound (*13*).

$$>C=O + RNH_2 \rightarrow >C(OH)NHR \quad (12)$$

$$>C(OH)NHR \rightarrow >C=NR + H_2O \quad (13)$$

Reactions with Ammonia[39–47]

In the reaction of ammonia with orthophthalaldehyde the formation of the carbinolamine follows dehydration to imine and its cyclization, yielding a reducible heterocyclic compound (*14*).



(*14*)

Reactions of ammonia with pyruvic acid also results in a cyclization yielding a reducible heterocycle.

Reactions of Carbonyl Compounds with Primary Amines[40,43,44,46–50]

These reactions yield in most instances an imine, which is also reduced at a more positive potential than the parent carbonyl compound. Examples of determined equilibrium constants are in Table I.

Reactions of Hydroxylamine[51–56] *and Hydrazine*[52,56–61] *with Carbonyl Compounds*

Hydroxylamine reacts with carbonyl compounds to yield an oxime, in which the four-electron electrode reduction is initiated by a two-electron cleavage of the single bond in the $N–OH_2^+$ group [(*15*)–(*19*)]. To be reducible at sufficiently positive potentials, protonation of the oxime takes place. The protonation takes place on adsorbed oxime and the resulting waves are neither suitable for determination of equilibrium constants nor for investigation of the homogeneous kinetics of the reactions accompanying the oxime reduction.

$$PhCR{=}N{-}OH + H^+ \rightleftarrows [PhCR{=}N{-}OH]H^+ \quad (15)$$

$$[PhCR{=}N{-}OH]H^+ + H^+ \rightleftarrows PhCR{=}NH^+OH_2^+ \quad (16)$$

$$PhCR{=}NH^+OH_2^+ + 2\ e \rightarrow PhCR{=}NH + H_2O \quad (17)$$

$$PhCR{=}NH + H^+ \rightleftarrows PhCR{=}NH_2^+ \quad (18)$$

$$PhCR{=}NH_2^+ + 2\ e + 2\ H^+ \rightarrow PhCRHNH_3^+ \quad (19)$$

$$PhCR{=}NHNH_2 + 2\ e + 2\ H^+ \rightarrow PhCR{=}NH + NH_3^+ \quad (20)$$

Hydrazine reacts with carbonyl compounds in an analogous way (*20*), followed by (*18*) and (*19*), where the protonation of the -NH_2- group takes place before the uptake of the first electron and cleavage of the N–NH_2 bond in the four-electron process. In reactions, yielding reducible hydrazones, it was possible to investigate the formation of the carbinolamine.

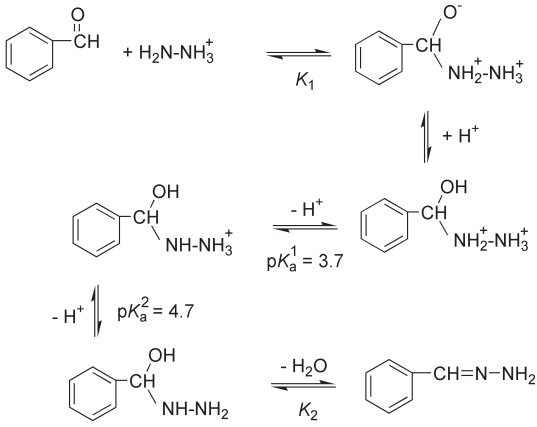
The limiting currents of the hydrazone and of the reacting carbonyl compound (such as benzaldehyde) were followed and the difference between the current of the starting material and the product have been observed.

TABLE I
Equilibrium constants K_c of reactions of aromatic aldehydes with 2-aminoethanol (RNH_2) and ammonia at 25 °C

Compound	Amine	K_c[a], l mol^{-1}	*n*	Technique
IPA[e]	RNH_2	4.1×10^2	30	polarography[b]
	NH_3	2.2×10^{-1}	6	polarography[b]
		2.8×10^{-1}[c]	8	
TPA[f]	RNH_2	6.2×10^2	11	spectrophotometry[d]
	NH_3	5.0×10^{-1}	6	polarography[c]
		4.5×10^{-1}[c]	8	polarography[c]

[a] K_1 = [imine]/[dialdehyde][RNH_2]; [b] polarography; [c] with μ = const.; [d] λ = 288 nm; [e] isophthalaldehyde; [f] terephthalaldehyde.

This difference corresponds to the concentration of the carbinolamine (Fig. 4). The dependence of the concentration of the carbinolamine on pH makes it possible to prove an involvement of three acido-basic steps in the conversion of the carbinolamine into the final hydrazone (*21*).



(*21*)

When the hydrazine was reacted with terephthalaldehyde, it was also possible to observe formations of carbinolamines (Fig. 4). When one of the carbonyl groups was converted into a carbinolamine, a separate wave was observed for the resulting benzaldehyde substituted in *para* position by the carbinolamine group. Similarly, it was possible to observe a formation of the second carbinolamine at a more negative potential.

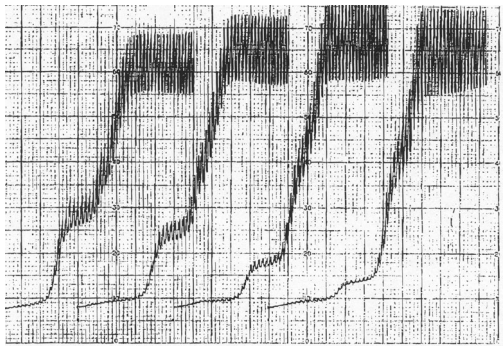


FIG. 4
Polarographic current-voltage curves recorded in a reaction of terephthalaldehyde with hydrazine. Concentration of hydrazine increases from right to left. Most positive wave: Reduction of the first formyl group of the dialdehyde; intermediate wave: reduction of the carbinolamine; most negative wave: reduction of the second formyl group of the dialdehyde.

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