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Electroanalytical evidence for the formation of carbinolamines in the reactions of terephthalaldehyde with hydrazine

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Abstract—Electroanalytical techniques enable the detection and following of time changes of three intermediates (two carbinolamines and one monohydrazone) in the reaction of terephthalaldehyde with hydrazine at pH 7.3.

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The formation of a carbinolamine as an intermediate in the reactions of carbonyl compounds with amines has been proposed without experimental evidence early.[1] Later an investigation of kinetics of the reaction of acetone with hydroxylamine indicated the presence of two reactions which have been attributed to the formation and the dehydration of the carbinolamine.[2] The observed pH-dependences of the second order rate constants were not interpreted. More recent investigations[3] of these types of reactions extensively used spectrophotometry to follow the kinetics of reactions of aromatic aldehydes and ketones. As the benzenoid absorptions in the 250–280 nm range of starting materials, reaction products and intermediates overlap, simultaneous quantitative following of concentrations of the starting material, intermediate, and product was not possible due to the unknown molar absorptivity of the intermediate in this region of the spectra. The use of the forbidden $n \rightarrow \pi^*$ transition involving the C=O group enables only a following of the decrease in the concentration of the carbonyl compound. Measuring the absorbance at about 250–270 nm in the solution of the carbonyl compound, immediately after addition of the nucleophile and after establishment of the equilibrium made it possible to offer qualitative information about the presence of the carbinolamine intermediate.[4]

We have recently demonstrated[5] that measuring limiting currents obtained by recording polarographic current–voltage curves using a dropping mercury electrode as a function of time, enabled in the reaction of benzaldehyde with hydrazine to simultaneously determine quantitatively concentrations of the parent aldehyde, the carbinolamine, and the hydrazone formed. An experimental evidence has been obtained in the presence of excess of hydrazine and at pH < 7, where the formation of an azine is negligible. Separate reduction waves of the aldehyde and the hydrazone made it possible to follow the concentration changes of these two components as a function of time. The difference in the known total initial concentration and the sum of instantaneous concentrations of the carbonyl compound and hydrazone yields the concentration of the carbinolamine. A similar principle has been reported earlier in an investigation of the hydrolysis of benzylideneaniline.[6] In this study, nevertheless, the pH-dependence of equilibria involving carbinolamine and the rates of their establishment has not been investigated.

Using the changes of polarographic limiting currents with time it was possible to find conditions when equilibria were established and to follow the pH-dependence of equilibrium constants of both the formation of carbinolamine and its dehydration. In this letter we shall demonstrate that the time changes of polarographic limiting currents enable following reaction intermediates even in a more complex reaction, such as the reaction of terephthalaldehyde with hydrazine.

In this case the kinetic study was limited to pH > 7, where hydrazine is present predominantly in the unprotonated form. The formation of azine was prevented by using an excess of hydrazine. At pH < 7 the reaction

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was complicated even at low concentrations (typically 0.1 mM) by the formation of a polymer in a consecutive reaction.

To demonstrate the power of this experimental approach, changes at a single pH value (7.3) are reported here. The variations of observed limiting currents (which are proportional to concentrations) were followed at a constant concentration of terephthalaldehyde (0.1 mM) and a varied concentration of hydrazine. The variations of five currents—i_1, i_2, i_{2A}, i_3, and i_4—with time were followed (Fig. 1). Waves i_1 and i_4 correspond to the reduction of two formyl groups in the parent terephthalaldehyde (A), each by a transfer of two electrons. Wave i_{2A} corresponds to an eight-electron reduction of the final dihydrazone (E). The patterns of time dependences of waves i_2 and i_3, where the current after reaching a maximum value decreases with time, indicate that these currents correspond to a formation and reduction of intermediates (B, C, D). In sequence 1

$$\underset{i_1,i_4}{A} \rightleftarrows \underset{i_3}{B} \rightleftarrows \underset{i_2}{C} \rightleftarrows \underset{i_2}{D} \rightleftarrows \underset{i_{2A}}{E} \tag{1}$$

intermediate C is the monohydrazone, which is reduced in a four-electron process to an amine, B corresponds to a carbinolamine bearing in 4-position a CHO group and D to reduction of a CH=O group in a carbinolamine with a CH=NNH$_2$ group in 4-position. Wave i_3 can be attributed to a two-electron reduction of a formyl group in carbinolamine B. This reduction occurs in a potential range in which the other *para*-substituted benzaldehydes are reduced. The shape of the time dependence of wave i_2 in the presence of 1 mM hydrazine (Fig. 1b) indicates that a reduction of more than one intermediate takes place at this potential. The maximum current corresponds to a transfer of 4.3 electrons. This current is attributed to the four-electron reductions of benzaldehyde hydrazones, bearing in 4-position a CH$_2$OH group (from reduction of the first formyl group) or a carbinolamine group (CH(OH)NHNH$_2$). The current might be further increased by a two-electron reductive cleavage of the 4-CH$_2$NH$_2$ group, formed in the reduction of the first hydrazone group.

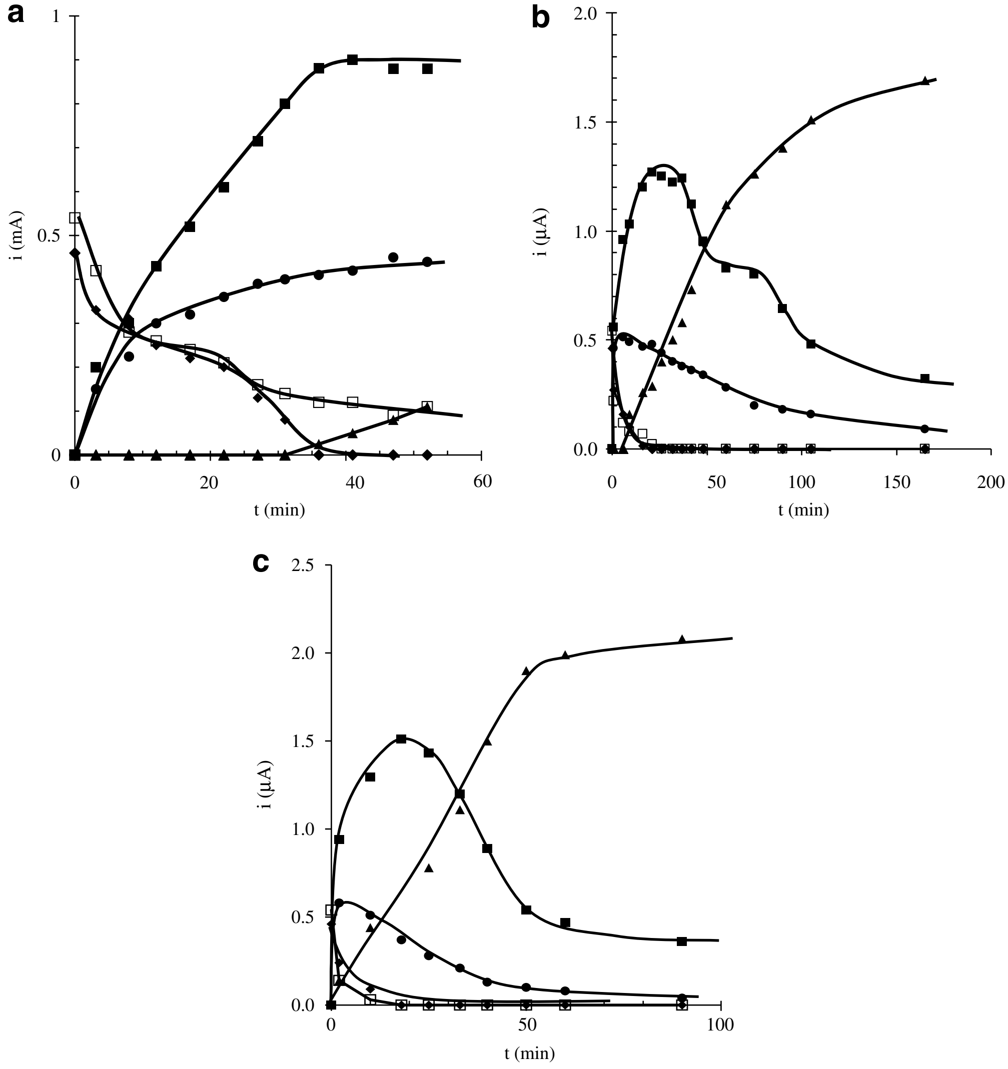

Figure 1. Time-dependence of limiting currents in a phosphate buffer pH 7.3 containing 1×10^{-4} M terephthalaldehyde and the following concentrations of hydrazine: (a) 2×10^{-4} M; (b) 1×10^{-3} M, and (c) 2×10^{-3} M. ◆i_1, ■ i_2, ▲ i_{2A}, ●i_3, □ i_4.

The proposed sequence 1 is supported by the sequence of reduction potentials $(E_{1/2})_1 < (E_{1/2})_2 < (E_{1/2})_{2A} < (E_{1/2})_3 < (E_{1/2})_4$. The equations for the dependence of half-wave potentials on pH are as follows: $(E_{1/2})_1 = 0.041\ \text{pH} + 0.46$, $(E_{1/2})_2 = 0.057\ \text{pH} + 0.41$, $(E_{1/2})_{2A} = 0.066\ \text{pH} + 0.41$, $(E_{1/2})_3 = 0.047\ \text{pH} + 0.79$, $(E_{1/2})_4 = 0.043\ \text{pH} + 0.92$.

In benzaldehyde and acetophenone the reduction of the carbonyl group takes place at more *negative* potentials than that of corresponding diprotonated hydrazones.[7] In terephthalaldehyde derivatives the sequence is different. The reduction of the first formyl group of terephthalaldehyde (A) occurs at more *positive* potentials than that of the reduction of the $\rangle C{=}NNH_2$ grouping in monohydrazone (C) in wave i_2. The reduction of 1,4-dihydrazone (E) occurs at even more negative potentials. This reflects the very strong resonance interaction observed[8] between the two 1,4-CHO groups. Such a strong resonance interaction does not operate between the two $\rangle C{=}NNH_2$ groups in dihydrazone E. A comparison of the reduction of monohydrazone C in wave i_2, which occurs at more positive potentials than the reduction of dihydrazone E in wave i_{2A}, indicates that the resonance effect of the 4-carbonyl group in C on the reduction of the 1-$\rangle C{=}NNH_2$ group is larger than the effect of 4-$\rangle C{=}NNH_2$ group in E.

A more detailed interpretation of processes in wave i_2 based on the investigation of pH-dependences of equilibria involving intermediates B, C, and D and of rates of their establishment is in progress.

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