

## Diprotonated hydrazones and oximes as reactive intermediates in electrochemical reductions

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**Abstract**—The shape of plots of limiting currents of some hydrazones and oximes as a function of pH, the slopes of  $E_{1/2}$ -pH plots (particularly for benzaldehyde *N,N,N*-trimethylhydrazonium ion) and the presence of separate two or three waves in reductions of some oximes bearing electron withdrawing groups represent a proof of formation of diprotonated forms of hydrazones and oximes as reaction intermediates. They are formed at the surface of the electrode in an equilibrium preceding the uptake of the first electron.

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The properties of diprotonated hydrazinium ions have recently been discussed<sup>1</sup> in a survey of chemistry of 1,2-dications. Formation and reactivity of diprotonated hydrazines was also considered to play a role in the rate determining steps of formation of  $\pi_2$ -products in benzidine rearrangement.<sup>2</sup> But the possibility of formation and reactivity of diprotonated hydrazones and oximes has—to our best knowledge—not been so far experimentally proven or considered. Similarly, no information has been reported concerning the existence and reactivity of diprotonated oximes.

In the course of our investigation of electroreductions of some hydrazones and oximes in aqueous buffered solutions, it was essential to elucidate the sequence of electron and proton transfers. Both hydrazones and oximes are known<sup>3–5</sup> to be reduced in a four-electron step, yielding amines. Decrease of the limiting current with pH increasing above about 7 indicated that a conjugated acid of the form predominating in the bulk of the solution is reduced.<sup>3–5</sup> It was also correctly recognized<sup>3,5</sup> that in the pH range, where the current decreases with increasing pH, the current is controlled by the rate of

protonation. Nevertheless, those observations of the dependence of current on pH were qualitative. In the absence of quantitative treatment there was no indication available about the number of protons transferred before the first electron uptake.

When proton transfers anteceding first electron transfer take place in a homogeneous reaction layer in the vicinity of the electrode surface, the limiting currents over the whole pH range remain independent of applied potential. For oximes and their derivatives<sup>4,6</sup> at a given pH the current–voltage curve obtained with a dropping mercury electrode decreases with increasingly negative potential. This indicates that the protonation occurs as a heterogeneous process at the electrode surface, where the amount of adsorbed conjugate base decreases with increasingly negative potential.

Reduction of an acid occurs invariably at a more positive potential than that of its conjugate base. The limiting current of a monobasic acid remains pH independent with increasing pH even over several pH units higher than  $pK_a$ , as long as the rate of protonation is sufficiently fast to convert all of the conjugate base present into the reducible acid form. The rate of protonation decreases with increasing pH and at a sufficiently high pH it will not be able to convert all of the present base into conjugate acid. The concentration of

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the acid in the vicinity of the electrode decreases with increasing pH and hence the current, governed by the rate of protonation, gradually decreases. The plot of  $i/i_d$  (where  $i_d$  is the diffusion controlled current at lower pH and  $i$  is the current controlled by the rate of protonation) as a function of pH is described by equation:

$$i_2/i_d = (\text{const.}[\text{H}^+]/([\text{H}^+] + K_2))/\{1 + (\text{const.}[\text{H}^+]/([\text{H}^+] + K_2))\}$$

where  $K_2$  equal to  $[\text{H}^+]$  where  $i_1 = i_d/2$ . For investigated hydrazones and oximes reductions of species richer by two protons than the species predominating in the bulk of solution, the corresponding plot follows:

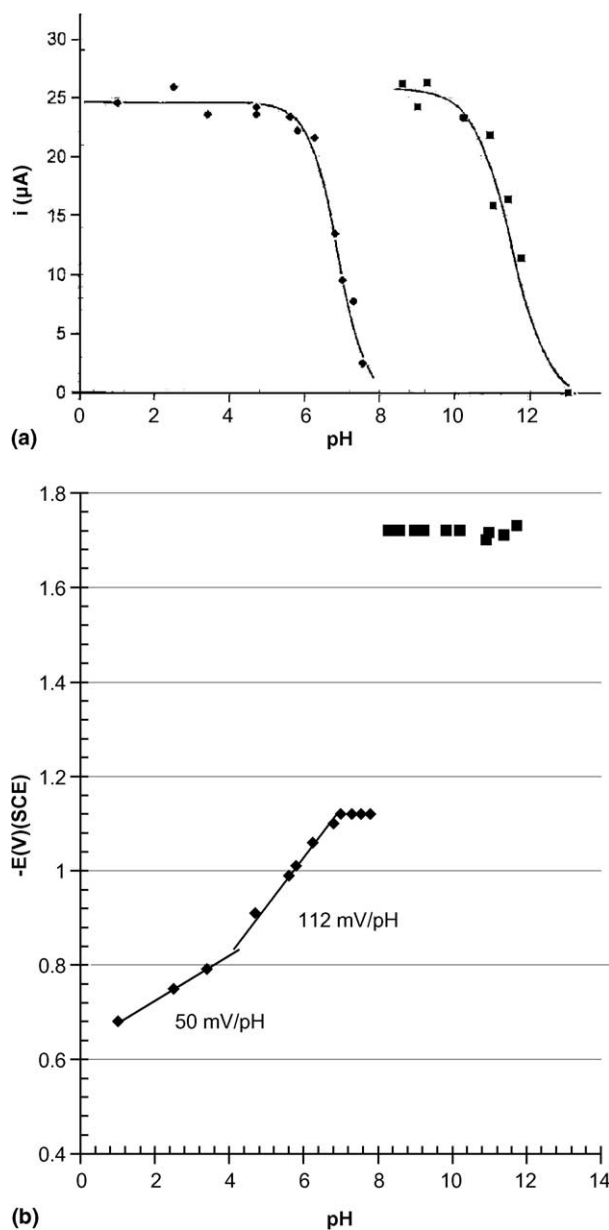
$$i_1/i_d = (\text{const.}[\text{H}^+]^2/([\text{H}^+] + K_1))/\{1 + \text{const.}[\text{H}^+]^2/([\text{H}^+] + K_1)\}$$

where  $K_1$  equal to  $[\text{H}^+]$  where  $i_2 = i_d/2$ . For both the monoprotonated and diprotonated species the plot of  $i/i_d = f(\text{pH})$  has a shape of a dissociation curve, the shape being steeper in the case of transfer of two protons. For reduction of a monobasic acid  $i$  decreases from 90%  $i_d$  to 10%  $i_d$  within two pH units (Fig. 1a). For cases, where transfer of two protons precedes the transfer of the first electron, the decrease from 90%  $i_d$  to 10%  $i_d$  occurs within a single pH unit. For investigated hydrazones and oximes, the shape of the  $i/i_d = f(\text{pH})$  plots indicated transfer of two protons before the transfer of the first electron.

Another proof for the antecedent transfer of two protons is given by the plots of potentials as a function of pH. The half-wave potentials are shifted to more negative values with increasing pH even for irreversible processes, due to additional energy needed for the proton transfer. The slopes of plots of  $E_{1/2} = f(\text{pH})$  usually indicate the numbers of protons transferred before the first electron transfer. Values of  $dE_{1/2}/dpH$  between 0.100 and 0.120 V/pH were observed for reductions of hydrazones, which indicate transfer of two  $\text{H}^+$  before the first electron uptake. Even more informative were plots of  $E_{1/2} = f(\text{pH})$  for oximes (Fig. 1b). These plots show two linear segments with slopes of about 0.050 V/pH at  $\text{pH} < \text{p}K_a$  and about 0.110 V/pH at  $\text{pH} > \text{p}K_a$  (where  $K_a$  corresponds to the dissociation constant of the monoprotonated form of the oxime—as confirmed by pH dependence of UV spectra). At  $\text{pH} < \text{p}K_a$  the monoprotonated form predominates in the solution and accepts a single proton before the electroreduction. At  $\text{pH} > \text{p}K_a$  the predominating unprotonated form takes up two protons before the transfer of the first electron.

For  $N,N,N$ -trialkylhydrazonium ions the half-wave potentials were also shifted to more negative potentials with increasing pH. The observed shifts of 0.056 V/pH corresponded to a transfer of a single proton preceding the first electron transfer. Thus even in these compounds the reducible form bears two positive charges on adjacent nitrogen atoms.

Finally, and perhaps the most convincing proof of reduction of the diprotonated form, is the presence and

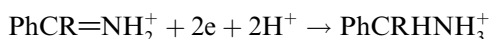
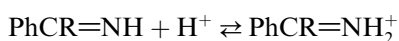
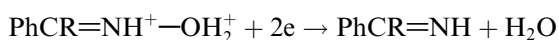
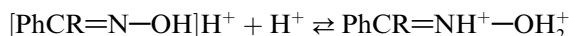
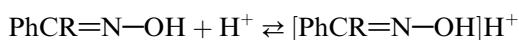


**Figure 1.** Reduction of 0.1 mM 4-trifluoromethylacetophenone oxime in buffered solutions containing 1%  $\text{CH}_3\text{CN}$  and 0.004% gelatin. (a) Dependences of limiting currents on pH. Left curve: Theoretical curve for reduction of a diprotonated species. Right curve: Theoretical curve for the reduction of a monoprotonated species. At  $\text{pH} < 9$  the quantitative evaluation of the reduction of monoprotonated form is prevented by the current of reduction of  $\text{H}^+$  from the buffer. The decrease of current at  $\text{pH} > 10$  indicates decrease in the rate of protonation of the unprotonated form. Its reduction wave is overlapped by the current of supporting electrolyte. (b) Dependences of half-wave potentials on pH for diprotonated ( $\blacklozenge$ ) and monoprotonated ( $\blacksquare$ ) forms of the oxime. Slopes of 50 mV/pH at  $\text{pH} < 3.8$  correspond to a transfer of one proton, that of 112 mV/pH at  $\text{pH} 3.8\text{--}7.0$  to a transfer of two protons before the first electron uptake.  $\text{p}K_a$  3.8 corresponds to the dissociation of the monoprotonated form of the oxime.

pH dependence of two or three reduction waves in solutions of some oximes. For most studied hydrazones and oximes the reduction of conjugate bases occurs at so negative potentials that it is more or less overlapped by the current of reduction of  $\text{H}^+$  ions from supporting

electrolyte. This prevents quantitative evaluation of their complete pH dependence. In the case of reductions of oximes with strongly electron-withdrawing groups, such as *p*-cyano-, *p*-trifluoromethyl-, and *p*-carbomethoxy-benzaldehydes and -acetophenones, their sufficiently positive reduction potentials enable following reductions of diprotonated, monoprotated and in some cases even unprotonated forms. In agreement with the theory discussed above, the plot of the decrease of the reduction current of the diprotonated form with increasing pH as well as that of the increase in current of the monoprotated form is twice steeper than the plot of the decrease of the current of the monoprotated and increase in current of the unprotonated form with increasing pH (Fig. 1).

Thus, the sequence of proton and electron transfers for the reduction of the diprotonated form at  $\text{pH} > \text{p}K_a$  is shown for oximes:



The electrochemical behavior of hydrazones and oximes is thus consistent with the formation of a dicationic form, present as a reactive intermediate at the surface of the dropping mercury electrode. The role of diprotonated forms of hydrazones and oximes in their acid catalyzed hydrolysis and some other nucleophilic attacks on azomethine bonds in such compounds are currently under investigation.

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