

Polarographic Reduction of Hydroxamic Acids

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Acethydroxamic acid and propionhydroxamic acid were polarographically reduced in aqueous alcoholic solutions of tetraethyl ammonium iodide.

Over a pH range from 4.7 to 9.5 two distinct waves occur. For the acethydroxamic acid the more positive one levels off in the prescribed manner, giving a very well defined wave. The half wave potential of the more negative one has so great negative value that erratic dripping or streaming of the mercury occurs and deranges the polarographic curve, which shows a maximum. The first wave was therefore found most suitable for practical analytical purposes and accordingly studied thoroughly. For the propionhydroxamic acid the first waves also show some tendency to form rounded maxima but are still sufficiently well defined for analytical purposes.

The values of the half wave potentials seem to be practically independent of the pH of the solutions until the pH has increased to about 10. For acethydroxamic acid the values with respect to the saturated calomel electrode lie about 1.7 V, for propionhydroxamic acid about 1.85 V.

The form of the curves seems to indicate that the reaction at the cathode is irreversible and we have therefore not found it expedient to calculate $I/(I_{dc}-I)$.

Our reason for studying hydroxamic acids is their general utility in organic analysis. They owe their analytical application to the fact that they may be identified by their formation of soluble, red to violet coloured ferric salts¹. Since esters are readily hydroxylaminolyzed in the presence of alkali, this reaction can also be employed as a test for esters. Being interested in instrumental analysis and especially in polarographic methods we wanted to use hydroxamic acids for polarographic determination of esters. The saturated aliphatic esters are not capable of producing polarographic reduction waves²⁻⁴, and can therefore not be polarographically determined as such. The hydroxamic acids, however, which may be looked upon as oximes of the original acids, ought to be polarographically reducible, inasmuch as the corresponding oximes lend themselves to polarographic methods⁴. The authors made many negative attempts at obtaining reduction waves for hydroxamic acids, in different buffer solutions, but were nevertheless convinced that the problem could be solved

if only a suitable supporting electrolyte could be found. It must give no hydrogen wave, and only contain components with greatly negative reduction potentials. We have found that hydroxamic acids are not electro-reducible within the potential range given by buffers containing alkali salts in aqueous solution, the only resulting waves obviously being hydrogen waves. Consequently we had to make use of tetraalkylammonium salts. We noticed that Bobrowa and Matwejewa⁵ by polarographic reduction of unsaturated esters had used tetramethylammonium iodide in alcoholic solution, and their curves show that the usable potential range reaches to about -2.5 V. For our experiments we used a supporting electrolyte consisting of 0.1 M $N(C_2H_5)_4I$ in 50% C_2H_5OH with 0.005% tylose. The pH was raised by addition of $N(C_2H_5)_4OH$. Trying to lower pH was inexpedient inasmuch as it only resulted in the reduction of hydrogen ions. Most measurements were carried out with a mercury pool anode. In order to get significant values of the half-wave potentials, however, some polarograms were recorded with a saturated calomel electrode as external anode. The hydroxamic acids studied were acethydroxamic acid and propionhydroxamic acid.

EXPERIMENTAL PROCEDURE

In these experiments a recording polarograph from Radiometer, Copenhagen, was used. Instead of the usual lead batteries an arrangement with NiFe batteries in series with a rectifier was employed. It gave high stability to the potential across the bridge. The usual precautions against oxygen interference were taken, a mixture of pure nitrogen and hydrogen being bubbled through the supporting electrolyte in the electrolysis vessel until it showed no trace of any oxygen wave. The solutions to be measured were kept under the inert gas, the flow of which was only stopped during the recording of the polarograms.

The acethydroxamic acid was prepared by Farmaceutisk Industri A/S and the propionhydroxamic acid by Dr. Else Kloster Jensen at *Sentralinstitut for industriell forskning*. Both acids were recrystallized several times to make sure that they were chemically pure. Their molar concentration in the electrolysis vessel during the analysis was of the order 10^{-3} . The pH of the solutions was measured at the start and at the completion of the experiments.

EXPERIMENTAL RESULTS

The polarographic waves were very distinct even without the use of counter current, which was found to be superfluous in this case.

For the acethydroxamic acid as well as for the propionhydroxamic acid the polarograms consist of two waves. Of these the first wave is the best defined reduction wave, while the second wave is apt to show a somewhat irregular behaviour that need not be ascribed to the hydroxamic acids, because the occurrence of variable and erratic drops is always apt to be troublesome in aqueous alcoholic solutions near the decomposition potential of tetraalkyl ammonium halides. The irregular form of the more negative wave therefore made us limit our efforts to the more positive one, as this wave lends itself readily to analytical purposes. Both waves were registered, but we find it adequate to render only the first one. For acethydroxamic acid the curves are given in Fig. 1. The curves all start at $V = 1.05$, and for each of them the curve for the corresponding supporting electrolyte was always taken.

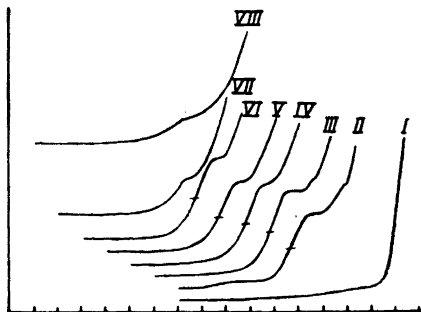


Fig. 1. Electro-reduction of the acethydroxamic acid at the pH values 4.7, 5.5, 6.5, 7.5, 8.5, 9.5 and 10.5, the pH increasing from curve II to curve VIII. Curve I represents the supporting electrolyte. Mercury pool anode.

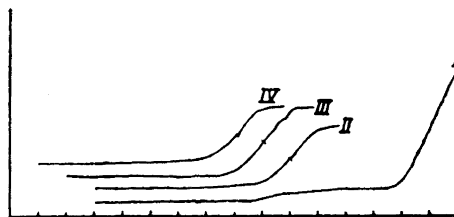


Fig. 2. Electro-reduction of acethydroxamic acid at the pH values 4.7, 7.0 and 9.0, the pH increasing from curve II to curve IV. Curve I represents the supporting electrolyte. Saturated calomel electrode as anode.

In order to express the half wave potentials with reference to the S.C.E., according to general practice, some records were made with a saturated calomel electrode as the second electrode. For the acethydroxamic acid the results are given in Fig. 2.

The value of the half wave potentials seemed to be independent of the pH except for the highest value, and referred to the mercury pool anode it was 1.7 V. Referred to the saturated calomel electrode it was 2.1 V in slightly acid solution and rose to 2.14 V only in distinctly basic solution.

The propionhydroxamic acid is also reduced in two steps. The first wave is apt to show a small rounded maximum. The second wave, on the other hand, is somewhat more regular than we were able to obtain it with the acethydroxamic acid. The value of the half wave potential as referred to the mercury pool was 1.8 V, versus the saturated calomel electrode 2.13 V.

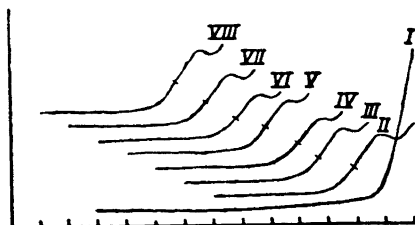


Fig. 3. Electro-reduction of propionhydroxamic acid at the pH values 4.7, 5.5, 6.0, 6.5, 7.0, 9.0 and 10.0, the pH increasing from curve II to curve VIII. Curve I represents the supporting electrolyte. Mercury pool anode.

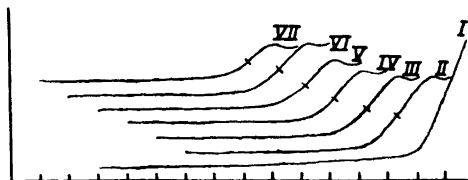


Fig. 4. Electro-reduction of propionhydroxamic acid at the pH values 4.7, 6.0, 7.0, 8.0, 9.5 and 10.5, the pH increasing from curve II to curve VII. Curve I represents the supporting electrolyte. Saturated calomel electrode as anode.

The results are given in Figs. 3 and 4. As a potential of 3 V had been laid across the bridge each interval on the abscissa represents 1.5 V. These curves were also started at 1.05 V.

DISCUSSION

If we compare the structure of the oxime tautomeric forms of the hydroxamic acids with the corresponding oximes, to wit: acethydroxamic acid $\text{CH}_3-\text{C} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{NOH} \end{array}$ with ethanal oxime $\text{CH}_3-\text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{NOH} \end{array}$, or propionhydroxamic acid $\text{CH}_3\text{CH}_2-\text{C} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{NOH} \end{array}$ with propanal oxime $\text{CH}_3\text{CH}_2-\text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{NOH} \end{array}$, we must be justified in assuming that a polarographic reduction will affect the double bond of the group $\text{>C} = \text{NOH}$ between the carbon and the nitrogen atom. Whereas the oximes have both weakly acid and weakly basic properties, the hydroxamic acids, on the other hand, are classed as acids in aqueous solution. This tends to make their reduction somewhat more sluggish and require a higher reduction potential. Even though they may be forced to accept electrons, this takes place polarographically only at relatively high negative potentials. As was to be expected, both the forms of the curves and the independence of the half wave potentials of the pH suggest irreversibility in the process.

The object of this investigation was to find an instrumental method for indication of the analytically very serviceable hydroxamic acids. This problem found its solution in a polarographic reduction of the acids in a supporting electrolyte consisting of a solution of tetraethyl ammonium iodide in an ethanol-water mixture. The curves were very well defined and always gave the same half-wave potential. This was practically independent of the pH of the solution, so that an addition of tetraethyl ammonium hydroxide seems superfluous.

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