

## Polarographic Investigation of Oximes as an Indication of the Polarographic Behaviour of Hydroxamic Acids

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The polarographic behaviour of several oximes has been investigated.

The oximes were readily reduced at the dropping mercury electrode giving well defined, reproducible waves.

The pH of the buffer used as supporting electrolyte influences the position of the half wave by shifting the half wave potential towards more negative values with increasing pH.

The form of the curves, and studies using the log plot method and the Ilkovic equation for determining the number of electrons consumed by the reaction, show that the reduction waves are irreversible.

The height of the polarographic waves decreases as the pH increases, indicating that neutral and alkaline buffers have insufficient protons for the reduction process.

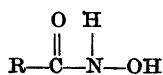
For some oximes double waves have been obtained within certain pH limits. Of the simple aliphatic monoximes only ethanal oxime gave a series of unmistakable double waves but in the case of 2,3-butanedione dioxime a number of polarograms exhibited pronounced double waves.

In the application of the polarographic method to organic problems greater difficulties are encountered than in the inorganic field. Consequently, the practical study of the polarographic reduction of organic compounds is still somewhat incomplete and many problems remain unsolved — among these is the determination of aliphatic esters. Although a direct polarographic reduction of simple saturated aliphatic esters seems out of the question, several attempts have been made. Thus Stackelberg and Stracke<sup>1</sup> investigated different types of organic compounds and found that ethyl acetate caused no rise of the polarographic curve as distinct from ethyl benzoate which gave a reduction wave with the half wave potential  $E_{\frac{1}{2}} = -2.14$ . Brdicka<sup>2</sup> concluded that ethyl acetoacetate is not reducible at the dropping mercury electrode. The present authors have endeavoured to obtain polarographic reduction with various saturated aliphatic esters by increasing the applied voltage as far as

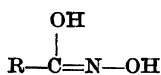
possible, but have concluded that such esters are not reducible within the potential range of the dropping mercury electrode.

Since direct polarographic reduction of the esters was impracticable an attempt was made to find readily prepared derivatives which would give well-defined reduction waves. The polarographic determination of these compounds might then be used to estimate the corresponding esters.

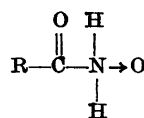
Primarily we were interested in the hydroxamic acids. The colour reaction between hydroxamic acids and ferric chloride was introduced by Feigl<sup>3</sup> as a spot test, but gives equally good results in macro analysis<sup>4,5</sup>. The hydroxamic acids with the molecular formula R—CO—NHOH are generally assumed to be tautomeric substances to which may be assigned the hydroxyamide structure (I) and the hydroxy-oxime structure (II). They may also be interpreted<sup>6,4</sup> as amide oxides (III).



(I)

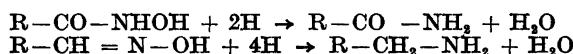


(II)



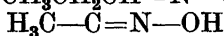
(III)

Both the hydroxy-amide group —CO—NHOH and the oxime group >C=N—OH have been chemically reduced by a variety of methods giving the corresponding amide, resp. amine for instance:

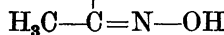


The hydroxamic acids, containing these groups, may, accordingly, be expected to undergo similar reductions. Moreover, if a simple oxime can be polarographically reduced yielding a distinct reduction wave it is possible that the hydroxamic acids themselves may also be polarographically reduced.

In order to test the above assumptions we first studied the polarographic behaviour of some simple aliphatic oximes, *viz.* ethanal oxime, CH<sub>3</sub>CH=N—OH, and propanal oxime, CH<sub>3</sub>CH<sub>2</sub>CH=N—OH. The diketone oxime, 2,3-



butanedione dioxime, was also tested. All these com-



pounds gave very well defined polarographic waves. As supporting electrolyte McIlvaine buffers were used within the pH limits 2.2 → 6.0. The reduction of two aromatic oximes, *viz.* the salicylaldehyde oxime, HO—C<sub>6</sub>H<sub>4</sub>—CH=N—OH,

and the ketoxime benzoin-1-oxime, C<sub>6</sub>H<sub>5</sub>—CHOH—C $\begin{array}{l} \nearrow \text{N}-\text{OH} \\ \searrow \text{C}_6\text{H}_5 \end{array}$

was also examined, and both of them were shown to give distinct waves.

The above mentioned measurements were carried out with a mercury pool anode, but some polarograms were also recorded using a saturated calomel electrode as external anode. Since the primary interest is in the aliphatic oximes these were re-examined in the case of ethanal oxime and propanal oxime and the investigation was supplemented by a study of 2-methylpropanal oxime.

## EXPERIMENTAL PROCEDURE

A recording polarograph (Radiometer, Copenhagen) was used in these experiments and for some of the records use was made of its counter current compensation arrangement. The usual precautions against oxygen interference were taken, the solutions in the electrolysis vessel being kept under an inert gas, the flow of which was stopped during the recording of the polarogram.

The molar concentrations of the oxime solutions were of the order  $10^{-3}$  to  $10^{-4}$ . The McIlvaine buffer solutions were prepared in the usual way and the oximes were not added until a polarogram showed that the buffer solution was oxygen-free — a suitable amount of the oxime solution in 50 % ethanol was then transferred to the polarographic cell. The pH of the solution was always determined at the start and controlled at the completion of the experiment.

## EXPERIMENTAL RESULTS

The records made applying counter current compensation gave very distinct polarographic waves. The aliphatic monoximes, however, showed a tendency towards the formation of maxima at pH values lower than 3; but when the pH values approached 4 the curves became completely regular. Conversely, the formation of maxima in solutions of aromatic oximes only appears at values of pH where the solutions can no longer be characterized as acid.

In addition to the chief wave some of the oximes show a small second wave with  $E_{\frac{1}{2}}$  at more negative voltages. This was the case for ethanal oxime within the pH limits  $5.4 \rightarrow 6$  but for propanal oxime, and for the two aromatic oximes, salicylaldehyde oxime and benzoin-1-oxime, only one wave was obtained. On the other hand 2,3-butanedione dioxime gives well pronounced second waves within the pH limits  $3.7 \rightarrow 5.4$ . Polarographic records of these experiments are given in Figs. 1—4.

The polarographic records for which the counter current compensation was omitted did not give such pronounced reduction waves as those already tabulated but they nevertheless confirmed the previous results. Since a saturated calomel electrode was used as external reference anode the half-wave

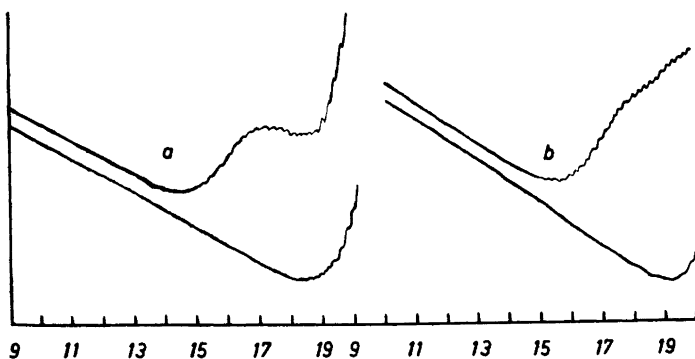


Fig. 1. Electro-reduction of ethanal oxime at pH = 4 and pH = 5.6,  $c = 6.5 \times 10^{-3}$ ,  $v_{appl} = 2$  V. Mercury pool anode, counter current. Only two of the polarograms are reproduced but data from the whole series are given in Table 1.

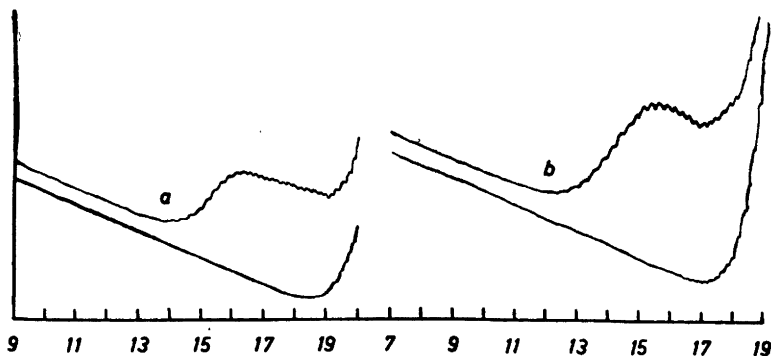


Fig. 2. Electro-reduction of propanal oxime at pH = 4 and pH = 5.6,  $c = 6.3 \times 10^{-3}$ ,  $v_{app} = 2$  V. Mercury pool anode, counter current. Complete data are given in Table 2.

Table 1. Half-wave potential and height of wave at different pHs for ethanal oxime,  $c = 6.5 \times 10^{-3}$ . McIlwaine buffer.  $l/sens = 300$ .

pH	$E_{1/2}^1$	$E_{1/2}^2$	$h_1$	$h_2$
2.2	1.54		41	
3.0	1.54		44	
3.6	1.58		48	
4.0	1.58		37	
5.0	1.68		33	
5.4	1.69	1.92	20	2.7
5.6	1.68	1.90	15	1.7
6.0	1.63	1.84	7	1.2

Table 2. Half wave potential and height of wave at different pHs for propanal oxime,  $c = 6.3 \times 10^{-3}$ . McIlwaine buffer.  $l/sens = 300$ .

pH	$E_{1/2}$	h
2.2	1.50	38
3.0	1.50	30
4.0	1.52	27
5.0		18.7
5.4		11.3
5.6		10.5
6.0		5.3

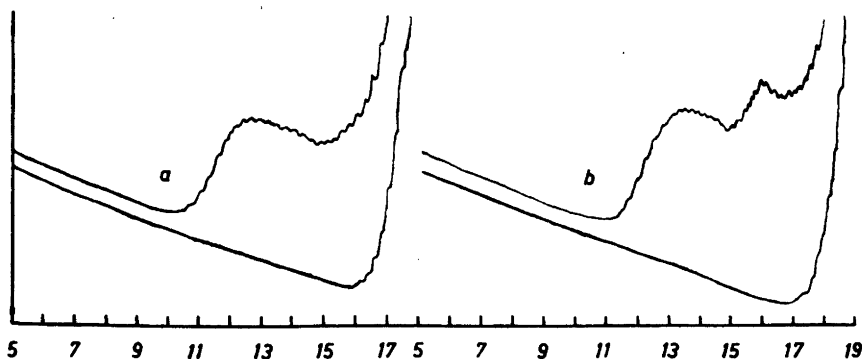


Fig. 3. Electro-reduction of 2,3-butanedione dioxime at pH = 3 and pH = 4,  $c = 2 \times 10^{-4}$ ,  $v_{app} = 2$  V. Mercury pool anode, counter current. Complete data are given in Table 3.

Table 3. Half wave potential and height of wave at different pHs for 2,3-butanedione dioxime,  $c = 2 \times 10^{-4}$ . Measured at  $1/\text{sens} = 15$ .

pH	$E_{1/2}^1$	$E_{1/2}^2$	$h_1$	$h_2$
2.2	1.08		65	
3.0	1.15		43	
3.6	1.22		46	
3.7	1.22	1.57	42	8
3.8	1.22	1.57	39	10
3.9	1.22	1.57	43	11.5
4.0	1.22	1.55	48	18
5.0	1.30	1.53	26	6
5.4	1.32	1.52	19	2
5.6	1.36		24	
6.0	1.38		21	

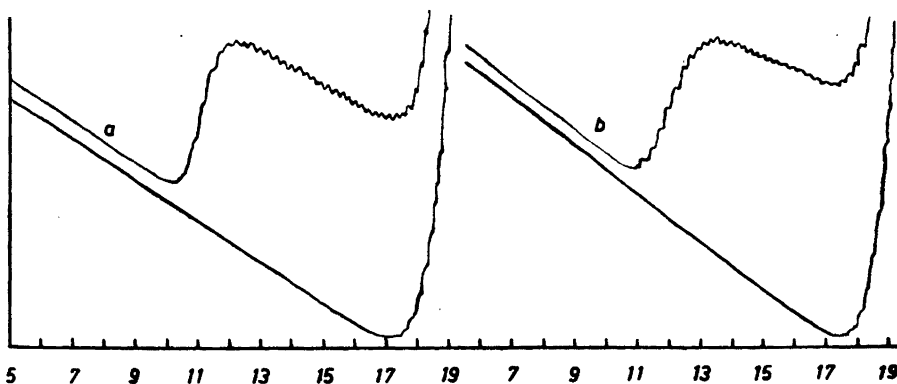


Fig. 4. Electro-reduction of salicylaldehyde oxime and of benzoin-1-oxime at pH = 4,  $c_a = 10^{-3}$ ,  $c_b = 2 \times 10^{-4}$ .  $1/\text{sens}$  for a = 30, for b = 5.

Table 4. Half wave potential and height of wave at different pHs for salicylaldehyde oxime,  $c = 1 \times 10^{-3}$ . Measured at  $1/\text{sens} = 30$ .

pH	$E_{1/2}$	h
2.2	1.17	50
4.0	1.12	62
5.4	1.14	28
6.0	1.15	19

Table 5. Half wave potential and height of wave at different pHs for benzoin-1-oxime, calculated for  $c = 2 \times 10^{-4}$  and  $1/\text{sens} = 5$ .

pH	$E_{1/2}$	h
2.2	1.07	62
3.0	1.05	53
4.0	1.17	62
5.0	1.17	64
6.0	1.22	38

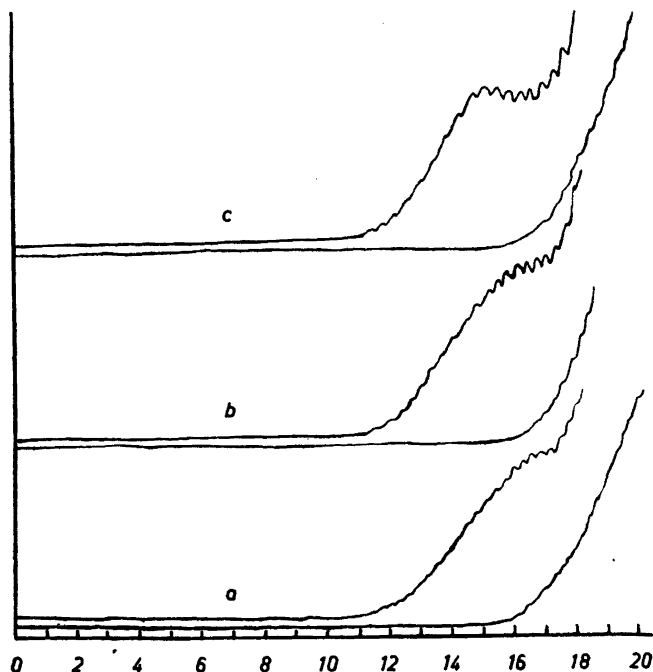


Fig. 5. Electro-reduction of ethanal oxime, propanal oxime and 2-methylpropanal oxime at  $\text{pH} = 5$ .  $c_a = 6.4 \times 10^{-3}$ ,  $c_b = 5.7 \times 10^{-3}$ ,  $c_c = 6.2 \times 10^{-3}$ . S.C.E. as reference electrode.

potentials were less negative in these latter curves than in the earlier ones and the tendency to form maxima was present at higher values of pH. The aliphatic oximes, ethanal oxime, propanal oxime and 2-methyl-propanal oxime, were examined in this way. A curve is given for each of these oximes (Fig. 5).

#### DISCUSSION

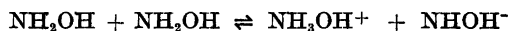
The polarographic records show that the electrolytic reduction of both aliphatic and aromatic oximes readily takes place in buffered solutions using the customary applied e.m.f. s and that very well defined waves are produced. Carruthers<sup>7</sup> obtained the same result when using salicylaldehyde oxime for the indirect determination of Cu, and good oxime curves were obtained by Kolthoff and Langers<sup>8</sup> during amperometric titrations of  $\text{Ni}^{++}$  with dimethylglyoxime (2,3-butanedione dioxime) and by Langers<sup>9</sup>, in the amperometric titration of copper with  $\alpha$ -benzoin oxime.

With increasing values of pH our half wave potentials showed a slight but regular shift towards more negative values indicating that the ease of reduction decreases slightly as the supporting electrolyte becomes less acid. Some of the oximes give a second wave as the acidity of the medium grows less.

Thus, as might be expected, the diketone dioxime shows double waves within certain pH limits. At pH = 3.7 the half wave potential values (against mercury anode) are  $-1.22$  V. and  $-1.57$  V. respectively, while at pH = 5.4 the heights of both waves have decreased, the second wave being hardly discernible and disappearing entirely at still higher pH values.

Double waves in connection with the polarographic reduction of organic substances occur frequently, and these are sometimes attributed to tautomerism or isomerism. Since oximes can show tautomerism as well as *cis-trans* isomerism these properties may be instrumental in producing anomalous waves. However, of the simple aliphatic aldehyde oximes, only ethanal oxime gave pronounced double waves and these did not appear until a pH of at least 5.4 was reached. Propanal oxime gave a very indistinct second wave at pH = 5.6.

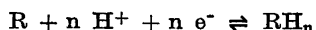
It is a well known fact that both the buffer system and the pH of the buffer influence the ease of reduction of organic substances. Thus many organic compounds which are weak bases may add protons from acid buffers and give more easily reducible compounds; this seems to be the case for the oximes inasmuch as the half wave potentials increase with increasing pH. It is to be expected that the ease of reduction of the oximes, which have both weakly acid and weakly basic properties, may depend on the pH of the solution, and it is possible that the substituted hydroxylamines exhibit auto-ionization corresponding to the well known autoionization of hydroxylamine itself:



In acid solution the hydroxylammonium form will predominate and it is not inconceivable that this form is the one most easily reduced since the wave height decreases with increasing pH of the supporting electrolyte, *i. e.* with a decreasing concentration of the hydroxylammonium form.

The fact that protons are used in the reduction of organic compounds also contributes to a more facile reduction in solutions of high hydrogen ion concentration.

For the reduction of organic substances one may write the general equation:



There are several methods for the determination of  $n$ . When the electrode reaction is reversible the log plot method has proved suitable. In our case, however, the form of the curves indicated that the electrolytic reduction of the oximes was an irreversible electrode reaction; calculations of  $\frac{v}{\log [i/(i_a - i)]}$  gave exceptionally high values while the slope of the log plot was much greater than that calculated for any probable value of  $n$ . Similarly, attempts to estimate  $n$  from the Ilkovic equation did not give reliable values with this method although Hartnell and Bricker<sup>10</sup> appear to have been successful in their calculations for methyl-4,5-diketo-2-pentenoate-5-oxime.

The authors are indebted to Bjørn Hansen and K. Maartmann-Moe for the recording of the polarograms.

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