

Polarographic Reduction of Aliphatic Esters

MILDA PRYTZ and TH. ØSTERUD

Yrkeshygienisk Institutt, Blindern - Oslo, Norway

Reaction mixtures of pure esters with hydroxylamine have been polarographed in ethanol-water solutions of tetra-*n*-butylammonium iodide, buffered with tetraethylammonium hydroxide. The resulting hydroxamic acid curves gave direct polarographic determinations of the aliphatic esters in question.

A series of esters were treated with an excess of hydroxylamine and sodium hydroxide in methanol solutions. After the reaction mixtures had been heated for fixed periods they were polarographed at room temperature and at different pH's with ethanol-water solutions of tetra-*n*-butylammonium iodide and tetraethylammonium hydroxide as supporting electrolyte.

We got distinct polarographic waves showing constant half wave potentials. These were for nearly related esters practically corresponding. Parallels without any addition of esters gave no analogous waves, *i.e.* the above mentioned curves have to be ascribed to the hydroxamic acid produced by the interaction of esters and hydroxylamine.

Esters have previously been determined colorimetrically as hydroxamic acids by Thompson¹. Our reaction mixtures did not differ essentially from his.

EXPERIMENTAL

A recording polarograph from Radiometer, Copenhagen (new model) was used. A mixture of nitrogen and hydrogen was passed through a chromochloride solution before it was bubbled through the electrolytic cell. For the heating of the reaction mixtures a water bath was used. Various concentrations of esters and of hydroxylamine as well as different lengths of time for heating of the reaction mixtures were tried. We fixed on a solution of ester in methanol, which was refluxed with a solution of hydroxylamine hydrochloride and sodium hydroxide in methanol in a water bath. The concentrations were as regards esters 0.04 M, as regards hydroxylamine hydrochloride 0.7 M and as to sodium hydroxide 3 M. Blank parallels without esters were also run. As supporting electrolyte was used a 0.1 M solution of (*n*-C₄H₉)₄NI from A. Frederick Smith, Columbus, Ohio, in a mixture of 50 parts of 95 % ethyl alcohol to 45 parts of water. In the electrolytic cell was added 9 drops of reaction mixture and some drops of tetraethylammonium hydroxide to 10 ml of the supporting electrolyte, and the pH was controlled. The tetraethylammonium hydroxide was either self prepared or obtained from the British Drug Houses. We found that a pH of about 12 gave the best curves. We had earlier found that the first hydroxamic

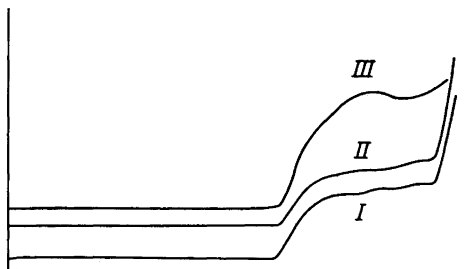


Fig. 1. Polarographic waves of acetic acid ethyl ester and of butyric acid ethyl ester at pH 12.6, Mercury anode.

- I. Acetic acid ethyl ester. Reaction mixture heated 1 h. Sens. 1.5×1000 .
- II. Acetic acid ethyl ester. Reaction mixture heated 2 h. Sens. 1.5×1000 .
- III. Butyric acid ethyl ester. Reaction mixture heated 1 h. Sens. 2×1000 .

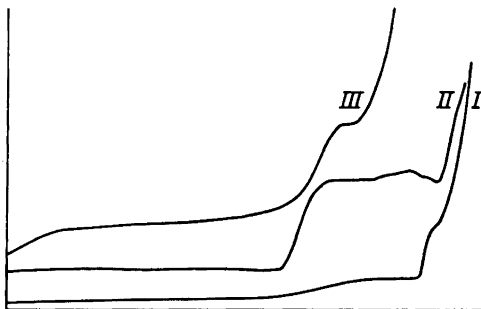


Fig. 2. Polarographic curves of:

- I. Blank test, heated for 1 h. Sens. 1.5×1000 , pH 12.6.
- II. Acetic acid isopropyl ester. Reaction mixture heated for 2 h. Sens. 1.5×1000 , pH 12.6.
- III. Propionhydroxamic acid. Sens. 7×10 , pH 12.6. Mercury anode.

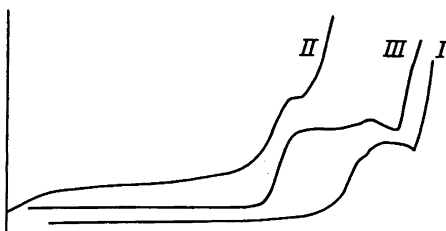


Fig. 3. Polarographic curves at pH 12.5 of:

- I. Acetaldoxime. Sens 5×100 .
- II. Propionhydroxamic acid. Sens. 7×10 .
- III. Acetic acid isopropyl ester. Sens. 1.5×1000 . Mercury anode.

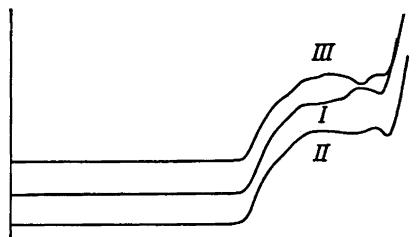


Fig. 4. Polarographic curves with S.C.E. anode of reaction mixtures heated for 1.5 h.

- I. Acetic acid isopropyl ester.
- II. Propionic acid ethyl ester.
- III. Butyric acid ethyl ester.

wave was most suitable for analytical purposes² and consequently we concentrated on that. For control some pure hydroxamic acids were polarographed in our present supporting electrolyte. In our polarographic investigation of oximes³ we used McIlvaine buffers. We therefore also determined the half-wave potentials of oximes in the above mentioned supporting electrolyte. We found that a mercury anode gave more reliable curves than a S.C.E. anode, as with use of the latter the cathode was apt to run. We therefore found the mercury pool anode more suited for practical analytical purposes in this connection, and only used the S.C.E. anode for recording of half wave potentials.

As a maximum depressor was used tylose, about 0.005 %.

RESULTS

Earlier investigations⁴ have shown that polarographic waves for hydroxamic acids in alkaline solutions were not affected, within reasonable limits, by time and heating, whereas polarographic waves for hydroxylamine in alkaline solutions decrease if the solutions stand for some time, and the decrease was greatly accelerated by heating. We therefore polarographed a series of reaction mixtures at different pH's, with varying excess of hydroxylamine, and with diverse lengths of time for heating, until we found the most favourable conditions for obtaining unmistakable and good waves. We decided on alkaline solutions with an excess of hydroxylamine of about 1 part of ester to 17.5 parts of hydroxylamine (molar conc.), and a time of heating of the reaction mixture between the limits 1 h and 2 h.

In Fig. 1 some curves are given for acetic acid ethyl ester (ethyl ethanoate) corresponding to acetylhydroxamic acid and of butyric acid ethyl ester (ethyl butanoate). In Fig. 2 are given curves for acetic acid *isopropyl* ester, corresponding to propionhydroxamic acid, as well as for a blank test.

Comparisons between oximes, pure hydroxamic acids and those produced in a reaction mixture seem to be indicated. A grouping of polarographic waves

Table 1. Polarographic half wave potentials of oximes and of pure hydroxamic acids and of converted esters at different pH's. Supporting electrolyte was $(n\text{-C}_4\text{H}_9)_4\text{NI} + (\text{C}_2\text{H}_5)_4\text{NOH}$ in equal parts of ethanol and water.

a. Mercury anode

b. S.C.E. anode

Compound	pH	Half wave potential, V	Compound	pH	Half wave potential, V
Acetaldoxime	8.8	2.00	Acetaldoxime	8.5	2.25
Acetaldoxime	11.6	2.04	Acetaldoxime	9.6	2.26
Propionhydroxamic acid	8.6	1.79			
Propionhydroxamic acid	10.8	1.79			
Acetic acid ethyl ester	12.6	1.67→ 1.70	Acetic acid ethyl ester	12.6	1.76
Acetic acid <i>isopropyl</i> ester	12.6	1.68→ 1.70	Acetic acid <i>isopropyl</i> ester	12.6	1.80
Butyric acid ethyl ester	12.6	1.69			

of an oxime, a hydroxamic acid and a reaction mixture in the supporting electrolyte used for this investigation is therefore given in Fig. 3. A mercury pool anode has been used.

As it might be of interest to record the half wave potentials with regard to the S.C.E. some determinations were made of ethyl esters of acetic acid and of propionic acid. Curves are given in Fig. 4.

Values of half wave potentials (under as similar conditions as possible as regards pH, supporting electrolyte and concentrations, and for esters time of heating) for oximes, for pure hydroxamic acids, and for reaction mixtures *i.e.* the corresponding esters are given in Table 1.

DISCUSSION

Our earlier observations that hydroxamic acids may be determined polarographically in alkaline solutions even if these originally contained some hydroxylamine⁴ have been the basis of the present investigation.

We have now been able to verify our assertions, even when hydroxamic acids are present in solution as a direct result of interaction between esters and hydroxylamine. As the reaction mixture was very simple to prepare, the excess of hydroxylamine was very easy to destroy without affecting the hydroxamic acid, and the polarographic curves were unmistakable, we dare claim to have found a serviceable method for direct polarographic qualitative determination of aliphatic esters.

Experiments of a more quantitative nature will be undertaken. The method will also be tested on ester-containing herbs.

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