Polarography and Reduction of Hydroxylamine-O-sulfonic Acid

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During a polarographic investigation of oxime-O-sulfonic acids it became of interest to investigate hydroxylamine-O-sulfonic acid, also called sulfoparomic acid. It was hoped that a polarographic investigation could throw light on the constitution of the compound in solution.

Hydroxylamine-N-sulfonic acid and hydroxylamine-N,N-disulfonic acid are not polarographically reducible \(^1\) and it was found here that hydroxylamine-O,N-disulfonic acid is not reducible between 0 and 2.0 V vs S.C.E. in buffered systems, whereas hydroxylamine-O-sulfonic acid is polarographically reducible. This difference is not surprising in view of the fact that hydroxylamine-O-sulfonic acid liberates iodine from iodide whereas the three aforementioned hydroxylaminesulfonic acids do not.

Hydroxylamine-O-sulfonic acid gives rise to a well-defined polarographic wave from pH about 2.5 to 14. Below pH 2.5 the wave is masked by the hydrogen wave. The half-wave potential of the compound is 1.28 V vs S.C.E. and it is independent of pH. The height of the wave suggests a two-electron reduction.

Controlled potential reduction at pH 9 shows the electrode reaction to be a two-electron reduction and the reduction products are ammonia and sulfate, the reaction thus being:

\[ \text{H}_2\text{N}^-\text{O}^-\text{SO}_4^{2-} + 2 \text{e}^- + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{SO}_4^{2-} + \text{OH}^- \]

Discussion. Several constitutions of hydroxylamine-O-sulfonic acid have been proposed and these have recently been reviewed by Wannagat and Pfeiffenschneider\(^2\). These authors conclude that hydroxylamine-O-sulfonic acid is an addition compound between SO\(_4\) and the amineoxide form of hydroxylamine, NH\(_3\)+-O-SO\(_4\)\(^2-\).

The result of the controlled potential reduction shows that the compound in buffered solution is not sulfamic acid N-oxide or an inner salt thereof \(^2\) as one would have expected the reduction product from such a compound to be sulfamic acid. This argument can be used against all formulations containing a nitrogen bonded directly to sulfur.

Hydroxylamine-O-sulfonic acid is a strong acid. In the pH-interval in which it is polarographically reducible it exists as the anion. Although some formation of undissociated acid might take place by recombination with hydrogen ions at the electrode surface this is not likely in strongly alkaline solution. The half-wave potential is independent of pH which makes it likely that it is the same species which is reduced in acid and alkaline solution and that it is the anion of hydroxylamine-O-sulfonic acid which is reduced. As the same anion, H\(_3\)N-O-SO\(_4\)\(^2-\), is formed from "hydroxylamine-O-sulfonic acid", H\(_2\)N-O-SO\(_4\)H, and from "ammonioxide sulfonic acid betain", H\(_3\)N\(^+\)-O-SO\(_4\)\(^2-\), the polarographic method can not be used to distinguish between the proposed formulations.

Hydroxylamine and derivatives of it like N-alkyl-, N-aryl- or O-alkylhydroxylamine are reduced at the dropping mercury electrode as the hydroxylammonium cation in a pH-dependent wave. In view of that, it seems difficult to explain why the hydroxylamine-O-sulfonic acid is not reducible in the protonated form, e.g. the betain, whereas the anion is. The easier reduction of the anion is in accordance with the fact found in a preliminary investigation that the reduction of hydroxylamine-O-sulfonic acid at 0°C by excess of iodide proceeded with a kinetics as a pseudomonomolecular reaction with a rate constant five times as high in an acetate buffer as in N hydrochloric acid.

Experimental. The polarograph was a recording polarograph Radiometer PO4d. The potentiostat was a Wadsworth Controlled Potential Electro-Depositor.

The rate of the chemical oxidation of iodide by hydroxylamine-O-sulfonic acid was found by continuous recording of the polarographic diffusion current of the iodine produced in the reaction. The potential of the electrode was kept at \(-0.7\) V vs S.C.E.

Reduction of hydroxylamine-O-sulfonic acid. 1.0 g of hydroxylamine-O-sulfonic acid was reduced in an aqueous buffer at 1.40 V vs S.C.E. The reaction required two electrons per molecule. After completion of the reduction the ammonia formed was distilled off, titrated and characterized as the benzoyl derivative, benzamidine. In the remnant sulfate was determined gravimetrically as barium sulfate. The yield of ammonia and sulfate was 91 % and 97 %, respectively.

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Electroorganic Preparations X. Polarography and Reduction of α-Naphthoic Acid

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Comparatively few compounds containing an ester or an amide group are polarographically reducible. Derivatives of the phthalic acids and of the pyridine mono- and dicarboxylic acids have been investigated polarographically and it has been found that the methyl esters of phthalic and terephthalic acid are reduced to phthalide \(^1\) and \(\gamma\)-hydroxymethylbenzoic acid methyl ester \(^8\), respectively, and that isonicotinic amide at pH 3 is reduced to \(\gamma\)-pyridyl carbinol \(^2\).

α-Naphthoic amide was found to be polarographically reducible and a controlled potential reduction was made in order to establish the nature of the reduction. α-Naphthoic acid yields a polarographic wave only in unbuffered or alkaline solution as the wave in acid solution is masked by the hydrogen wave. Only solutions containing lithium or tetraalkylammonium ions as supporting electrolyte can be used. In unbuffered 0.2 M tetraethylammonium bromide solution containing 40 % alcohol the half-wave potential is 1.88 V vs S.C.E.

By a controlled potential reduction it was shown that the reduction consumed 2 electrons per molecule and a product with m.p. 150° and an analysis corresponding to \(C_\text{H}_\text{H}_\text{NO}\) was obtained. The elementary analysis suggested a reduction in the naphthalene ring rather than in the amide group, the product thus being a dihydro-naphthoic amide. As the reduction most probably would take place in the ring to which the amide group was bonded and the melting points of 1,2-dihydroanaphthoic amide-1, m.p. 200°, and 3,4-dihydroanaphthoic amide-1, m.p. 185° or 128°, differed considerably from that of the isolated compound, the product might probably be 1,4-dihydronaphthoic amide-1 which apparently has not been described before.

In order to prove that, 1,4-dihydronaphthoic acid-1, m.p. 88°, prepared according to Baeyer \(^4\), was treated with thionyl chloride and the resulting chloride in benzene solution treated with concentrated aqueous ammonia. The compound formed had m.p. 150° and an infrared spectrum identical with that of the product obtained from the electrolytic reduction.

The UV-spectrum of the supposed 1,4-dihydronaphthoic amide, max. at 267 m\(\mu\) and 273 m\(\mu\) with \(\varepsilon_\text{max} 620\) and \(\varepsilon_\text{max} 570\) confirmed that no migration of the double bonds had taken place during the preparation from the acid, as 1,2- and 3,4-dihydronaphthoic amide would be expected to show a strong absorption (\(\varepsilon\) about 10\(^4\)) around 250 m\(\mu\) similar to that of styrene.

The polarographic reduction of α-naphthoic amide in alkaline solution is thus a 1,4-addition to the naphthalene ring. The reduction with sodium amalgam often resembles the reduction at a mercury electrode, but a reduction of α-naphthoic amide with sodium amalgam in acid solution yields α-naphthyl carbamol. The reduction thus takes place at different positions in acid and alkaline solution. This is also found in the polarographic reduction of isonicotinic amide which in acid solution is reduced in a four electron reduction to \(\gamma\)-pyridyl carbinol \(^8\) and in alkaline solution yields a two-electron wave indicating the formation of a dihydropyridine derivative.

Experimental. The polarograph was a pen-recording polarograph Radiometer Polaris P04d. The potential/timer was an electromechanical potentiostat of the Lingane-Jones type. The melting point determinations were made with a Leitz "Mikroskop-Heiztisch 350". The infrared spectra were recorded at a Perkin-Elmer Infracord and the UV-spectra with a Perkin-Elmer UV-137.

Reduction of α-naphthoic amide. 2.0 g of α-naphthoic amide was suspended in 180 ml 50 % methanol containing 5 g of lithium chloride and 2 g of tetramethylammonium hydroxide and reduced at −1.90 V vs S.C.E. The compound dissolved during the reduction which required two electrons per molecule. After completion of the reduction the solution was made slightly acidic with acetic acid and the main part of the methanol was removed in vacuo. The product was extracted from

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