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Electroörganic Preparations

XVIII. Preparation and Polarographic Determination of some *N*-Alkylhydroxylamines

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A cell for macroscale electrolytic reductions at controlled cathode potential is described and applied to the synthesis of some *N*-alkylhydroxylamines by reduction of the corresponding nitroalkanes. A polarographic determination of alkylhydroxylamines has been developed.

In the synthesis of *N*-alkylhydroxylamines from nitroalkanes by reduction with zinc [1–3] or by electrolytic reduction [4,5] only moderate yields (less than 50 %) have been obtained. The diborane reduction of oximes [6] gives high yields of some higher homologs, but moderate yield of methylhydroxylamine. In the present work electrolytic reductions at controlled potential have been applied to the synthesis of alkylhydroxylamines using considerably higher concentrations and currents than previously in this series of investigations.

Nitromethane, nitroethane, and 1- and 2-nitropropane have been reduced under controlled conditions in 3 N hydrochloric acid containing alcohol at 20°C at a stirred mercury electrode in the three-electrode cell described below. The yields of alkylhydroxylamines and alkylamines are given in Table 1.

Table 1. Results from electrolytic reduction of nitroalkanes at 20°C.

R	Amount of RNO_2	Analysis of catholyte			Current yield, %	% Isolated RNHOH
		% RNHOH	% RNH_2	% RNO_2		
Me	28.2 g	89	3.6	1.2	92.6	77
Et	31.1 g	82	9.9	0.8	92.9	59
1-Pr	40.1 g	83	5.9	1.2	91.6	62
2-Pr	39.7 g	86	4.6	0.8	90.5	81

The *N*-alkylhydroxylamines in the catholyte were determined by the anodic polarographic procedure described below. The alkylamine content was estimated by the method of Leeds and Smith [5] and the nitroalkanes by cathodic polarography.[7] *N*-Methylhydroxylamine was isolated as the hydrochloride and the other compounds as the free hydroxylamines using essentially the procedure of Ryer and Smith.[8]

Contrary to the findings of Leeds and Smith [5] the results in Table 1 show that the use of high current densities does not lower the yield of alkylhydroxylamines as long as the cathode potential is kept below the decomposition potential of the medium.

During the preparation and isolation of the hydroxylamines a control of the temperature is important in order to obtain a high yield of a colourless product. Reduction at 0° gives slightly higher yield of methylhydroxylamine (81 % isolated), but requires a very efficient cooling when currents of about 15 A are used, so for practical work reduction at room temperature is recommended.

The three-electrode cell employed is a modification of one used previously by one of us.[9] The anode compartment in the centre is rather small and the use of large quantities of electricity and high current densities makes a continuous renewal of the anolyte necessary.

The current yield is lowered to about 92 % by the simultaneous reduction of some hydrogen ions. This is due to a lowering of the hydrogen overvoltage in the presence of high concentrations of the reduction products and by differences in the cathode potential at various points of the rapidly stirred cathode. Such differences would be most pronounced at high current densities.

The selectivity of a controlled potential reduction is lowered by the use of high concentrations and current densities compared to the selectivity of the polarographic method. Several factors are responsible for this. In order to estimate this effect trichloroacetic acid has been reduced to dichloroacetic acid at controlled potential in a solution initially containing about 20 % trichloroacetic acid. The medium was an ammonia/ammonium chloride buffer, which previously has been used by Urabe, Seyama and Sakai.[10] Dichloroacetic acid was isolated in a yield of 74 %.

However, although the selectivity of the method is lowered somewhat by the use of high concentrations of the reducible compound and of high current densities the yields obtained above show that even under these conditions a control of the cathode potential is preferable to a control of the current density.

POLAROGRAPHIC DETERMINATION OF ALKYLHYDROXYLAMINES

Methylhydroxylamine has been determined by oxidation with a hot Fehling's solution;[5,11] Brady and Goldstein,[12] however, found the reaction irreproducible and non-stoichiometric and developed an iodometric titration. Cyclohexylhydroxylamine [13] has been determined by anodic polarography in a borax solution.

Hydroxylamine can be determined in several ways such as by visual [14] and potentiometric [15] titration, coulometry,[16] gasometry,[17] cathodic polarography,[18] and spectrophotometry.[19]

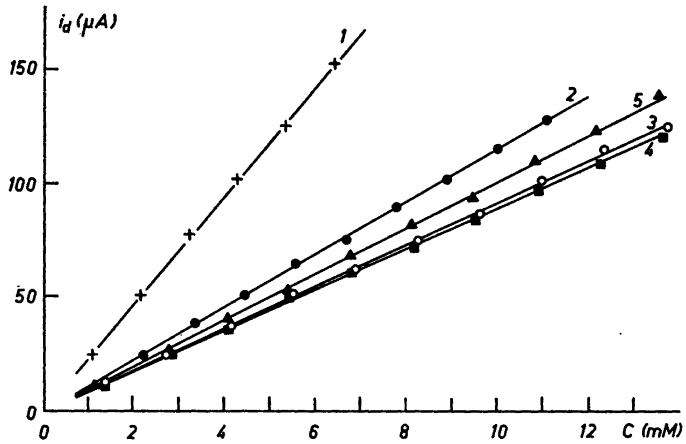

Fig. 1. Dependence of the anodic wave-height on the concentration of some alkylhydroxylamines in an alkaline 0.16 M sodium sulphite solution at pH 13. + Hydroxylamine, ● *N*-methylhydroxylamine, ○ *N*-ethylhydroxylamine, ■ *N*-propylhydroxylamine, ▲ *N*-isopropylhydroxylamine.

Alkylhydroxylamines yield polarographically an ill-defined cathodic wave at intermediate pH-values;[7] this wave is not suited for a quantitative analysis as it occurs at a potential too near the decomposition potential of the medium. The anodic wave found in alkaline solution is, however, well-defined and a determination of alkylhydroxylamines has been developed using this anodic wave.

In the presence of oxygen the alkylhydroxylamines yield an irreproducible, anodic double-wave, which cannot be removed by flushing with nitrogen; furthermore, the lowest homologues are somewhat volatile. Instead, the oxygen is removed by using an alkaline solution of sulphite as supporting electrolyte; in this medium a single, well-formed wave suitable for a quantitative determination of hydroxylamine and the alkylhydroxylamines is produced.

A linear dependence is found between the wave-height and the concentration of alkylhydroxylamine in the range 10^{-4}—10^{-2} M (Fig. 1). Experimental points around 10^{-4} M indicate a slight curvature with the result that the curve does not pass through the origin. The reason for this is not known.

The limiting current is diffusion controlled as the wave-height is proportional to the square root of the height of the mercury reservoir. The dependence of the wave-height on the concentration of potassium hydroxide and sodium sulphite is only slight in the chosen range. The wave-height has been found reproducible within 1—2 %; the accuracy is estimated to 2—3 %.

The half-wave potentials of hydroxylamine and alkylhydroxylamines are given in Table 2 together with the diffusion current constants. The difference between the half-wave potentials of hydroxylamine and that of an alkylhydroxylamine is great enough to permit a simultaneous determination of the two species, when their concentrations are of the same order of magnitude.

Table 2. Half-wave potentials (*vs.* S.C.E.) and diffusion current constants of some alkylhydroxylamines in an alkaline sulphite solution at pH 13. Concentration of hydroxylamines 10^{-3} M.

R	H	Me	Et	1-Pr	2-Pr
$E_{\frac{1}{2}}$	−0.32	−0.45	−0.45	−0.45	−0.45
$\frac{i_d}{cm^{2/3}\, t^{1/6}}$	8.69	4.21	3.36	3.25	3.73

The simultaneous determination of hydroxylamine and an alkylhydroxylamine is not possible with any of the previously described methods; the accuracy, however, decreases somewhat relative to a determination of a single compound.

A comparison of the wave-height of *N*-methylhydroxylamine at low concentrations with that of *N*,*N*′-dimethylhydrazine, which is oxidised to azomethane in a two-electron reaction, suggests that the anodic wave of *N*-methylhydroxylamine is caused by a two-electron oxidation. This would correspond to an oxidation of methylhydroxylamine to nitrosomethane. A preparative oxidation at a potential controlled at −0.15 V *vs.* S.C.E. of a 0.085 M solution of *N*-methylhydroxylamine consumed, however, 1.1 electrons per molecule and produced azoxymethane, which may be formed in the reaction between nitrosomethane and *N*-methylhydroxylamine, and other products. A similar concentration dependent electron consumption has been found, *e.g.* in the anodic oxidation of hydrazine.[20]

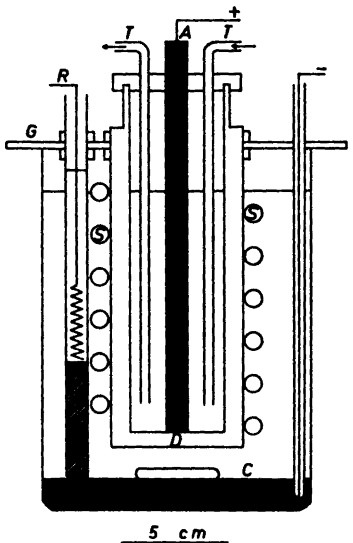

Fig. 2. Cell for macro-scale electrolysis at controlled potential.

EXPERIMENTAL

The polarograph was a recording polarograph Radiometer PO4d. The capillary delivered 3.81 mg of mercury at a corrected mercury column height of 48.6 cm. The drop time was 2.81 sec (water, open circuit). The cathode potential was measured with a vacuum-tube voltmeter and the quantity of electricity with an electromechanical integrator. The cathode potential was initially controlled manually and at the later stages of the reduction eventually with a potentiostat, a Wadsworth Electrodepositor.

The cell (Fig. 2) consists of a 2 l beaker covered with a glass plate G containing holes for a silver/silver chloride reference electrode R, the anode compartment, a cooling coil S, a thermometer, an inlet for nitrogen, and one for withdrawing of samples. The mercury cathode C has an area of 125 cm^2, it is stirred magnetically. The diaphragm D between the anode and cathode compartments consists of two porous clay cylinders separated by agar containing potassium chloride. The anolyte (15 % aqueous sodium hydroxide) is continuously renewed through the tubes T, and by suitable adjustment of the flow-rate the stainless steel anode A is not attacked even at high current densities.

The nitroalkanes were middle fractions with satisfactory boiling range and index of refraction obtained by fractionating the commercially available compounds through a 30 cm column. The microanalyses were made by the Microanalytical Laboratory of Dr. Weiler & Dr. Strauss, Oxford, and our Analytical Department.

Reduction of nitromethane. In a pre-electrolysed catholyte consisting of 200 ml of conc. hydrochloric acid, 500 ml of water, and 100 ml of 96 % ethanol, 25.0 ml (28.2 g) of nitromethane were introduced and reduced at a cathode potential not below −0.85 V *vs.* S.C.E. at 15°−20°. After 8 h, in which the initial current of 15 A had dropped to about 0.4 A and approximately the theoretical amount of electricity (4 F/mole) had been consumed, the colourless or slightly yellowish catholyte was diluted to 1000 ml with water, samples were withdrawn for analysis, and the remaining solution was evaporated *in vacuo* at temperatures not exceeding 50°. The residue was triturated twice with 50 ml of absolute alcohol, which were evaporated *in vacuo*, and extracted with absolute alcohol at room temperature yielding a yellowish solution. Most of the solvent was removed *in vacuo* at temperatures not exceeding 35° and on cooling of the remainder to −10° *N*-methylhydroxylamine hydrochloride crystallised in white needles, which were filtered off, washed with cold absolute alcohol and ether, and dried *in vacuo* over calcium chloride; 22.4 g, m.p. 87°−88°. By concentrating the mother liquor further 7.5 g, m.p. 83°−85°, were obtained. Total yield 77 %. After two recrystallisations from a 2:1 mixture of ethanol-chloroform, m.p. was 88°−89° (m.p. 87°).[3] (Found: C 14.41; H 7.50; N 16.38. Calc. for CH_6NOCl: C 14.39; H 7.24; N 16.79. Equiv. wt. of chloride: Found: 83.5. Calc.: 83.5).

Reduction of nitroethane. 30.0 ml (31.5 g) of nitroethane were reduced in a pre-electrolysed catholyte consisting of 200 ml of conc. hydrochloric acid, 300 ml of water, and 300 ml of 96 % ethanol. The cathode potential was kept not below −0.90 V *vs.* S.C.E., the temperature not above 22°. The reduction and the evaporation of the solvent were performed as described above. To the residue was added a large excess of anhydrous potassium carbonate and the free ethylhydroxylamine extracted with 300 ml of hot ether. The solution was filtered hot, cooled to about −80°, the precipitate of white flakes filtered off and dried *in vacuo* over potassium hydroxide. The mother liquor was used twice for further extractions. Isolated were 15.1 g (59 %) of *N*-ethylhydroxylamine, m.p. 54°−56° (closed tube). The compound was purified by vacuum sublimation at 35°/10 mm, m.p. 55°−56 (55°−56°).[3] The pure alkylhydroxylamines seem stable at room temperature when kept in a well-stoppered container, but should preferably be stored at low temperatures.

The oxalate was prepared according to Ryer and Smith [8] and recrystallised twice from methanol, m.p. 107°−108°. (Found: C 34.17; H 7.34. Calc. for $C_6H_{16}N_2O_6$: C 33.95; H 7.60. Acid equiv. wt.: Found: 105. Calc.: 106.1).

Reduction of 1-nitropropane. 40.0 ml (40.1 g) of 1-nitropropane were reduced and isolated as described for nitroethane, except that the free hydroxylamine was extracted with petrol ether, b.p. 40°−60°. Yield 20.9 g (62 %), m.p. 40°−42° (closed tube). The *N*-propylhydroxylamine was purified by vacuum sublimation at 35°/10 mm, m.p. 45°−46° (45.5°−46°).[8] Oxalate, m.p. 153°−154° (154°−155°).[8] (Found: C 40.28; H 8.49; N 11.90. Calc. for $C_8H_{20}N_2O_6$: C 40.00; H 8.39; N 11.66. Acid equiv. wt. Found: 120.3. Calc.: 120.1).

Reduction of 2-nitropropane. 40.0 ml (39.7 g) of 2-nitropropane were reduced and the hydroxylamine isolated as described for nitroethane, except that the free hydroxylamine was extracted with ligroin, b.p. 100°—140°. Yield 27.1 g (81 %), m.p. 80°—82°. The *N*-isopropylhydroxylamine was purified by vacuum sublimation at 45°/10 mm, m.p. 86°—87° (86°—87°).[8] Oxalate, m.p. 157°—158° (159°—160°).[8] (Found: C 40.03; H 8.36. Calc. for $C_8H_{20}N_2O_6$: C 40.00; H 8.39. Acid equiv. wt.: Found: 120.5. Calc. 120.1).

Reduction of trichloroacetic acid. 163.4 g (1.0 mole) of trichloroacetic acid were reduced in a solution containing 500 ml of water, 100 ml of 25 % aqueous ammonia, and 200 g of ammonium chloride at a cathode potential not below −1.25 V *vs* S.C.E. After the passage of slightly more than 2 F trichloroacetic acid was not detectable polarographically in samples withdrawn from the catholyte. The catholyte was made strongly acid with conc. hydrochloric acid and extracted continuously for 40 h with ether. The extract was dried over sodium sulphate, filtered, and the ether removed. The residue was fractionated *in vacuo*, and 94.8 g (73.5 %) of dichloroacetic acid, b.p. 85°—85.5°/10 mm, were obtained. $n_D^{23} = 1.4660$ ($n_D^{22} = 1.4659$).[21]

Polarographic determination of N-alkylhydroxylamines. 1.0 ml of a solution containing 0.5—5 mg of alkylhydroxylamine per ml is diluted to 25.0 ml with a solution containing 20 g of sodium sulphite and 9 g of potassium hydroxide per litre. The solution may be polarographed from 0.0 to −0.7 V *vs.* S.C.E. shortly after the mixing of the solutions, and the wave-height compared with that of a standard solution under the same conditions. The hydrochlorides of hydroxylamine and its *N*-methyl derivative and the oxalates of *N*-ethyl-, *N*-propyl-, *N*-isopropylhydroxylamine were used as standards.

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