ELECTROCHEMICAL SYNTHESIS OF UN-SYMMETRICAL N.N-DIISOPROPYLHYDRAZINE

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N,N-diisopropylhydrazine has been prepared by electrolytic reduction of N,N-diisopropylnitrosamine in alcoholic medium using hydrochloric acid as supporting electrolyte. The influence of (1) cathodic material (2) catholyte composition and (3) temperature on the yield of the reduced product has also been studied. A plausible mechanism of the reduction has been proposed.

Unsymmetrical hydrazines are of immense importance because of their use as propellant in rockets <1>. A survey of literature reveals many conventional chemical methods for the preparation of unsymmetrical N, N-dialkylhydrazines <2>. The electrolytic preparation of the unsymmetrical dialkylhydrazine was first reported by Cook et al <3>. Lund <4> and Marten <5> studied their behaviour on DME in aqueous sulphuric acid. Russian authors<6> have also studied the electrolytic preparation of unsymmetrical dialkylhydrazines in mineral acid using high hydrogen overvoltage metals like lead.

Udupa et al <7> have reported the optimum conditions for the preparation of unsymmetrical dimethylhydrazine in aqueous medium using rotating Pb and Cu cathodes and H_2SO_4 as supporting electrolyte.

In the present communication we report a simple, efficient and comparatively better electrochemical method for the reduction of N,N-diisopropylnitrosamine to the unsymmetrical N,N-diisopropylhydrazine using a divided cell with porous diaphragm<8-9>.

EXPERIMENTAL

Materials

N,N-diisopropylamine (FLUKA) was used without further purification. The corresponding nitroso derivative was prepared by the reported method <10>. HCl used was of laboratory grade. EtOH and MeOH (L.R.) were distilled and dried prior to use.

Cell Assembly

Cell assembly was the same as used earlier <8,9>. Hg, Cu and Pb were used one by one as cathode material and Pt foil inside the diaphragm served as anode in each case. All the experiments were carried out at 0.3 Ampere (c.d. = 0.0078 Amp/cm^2).

Electrolysis and Work Up

Details of electrolysis set up are as follows: Catholyte -100 ml alcoholic solution of 5×10^{-3} M N,N-diisopropylnitrosamine containing 5, 10, 15 or 20%. HCl (v/v as supportivng electrolyte).

Anolyte-40 ml 10% (v/v)HCL IN EtOH or MeOH

After passing the current for the calculated time corresponding to 4F/mole, the catholyte was filtered and the filtrate was evaporated on a water bath to the point of crystallisation. After cooling the contents of the flask, needles of N,N-diisopropylhydrazine hydrochloride separated out. These were filtered and dried at vacuum pump. The yield of the product in different experiments is presented in (Table 1-3). The characterization of the product, N,N-diisopropyl hydrazine hydrochloride has been done by elemental analysis (Found: C, 47.4; H, 11.8; N, 17.5 calculated: C, 47.2; H, 11.1; N, 18.4).

RESULTS AND DISCUSSION

The electrolytic reduction of N,N-diisopropylnitrosamine (1) to N,N-diisopropylhydrazine hydrochloride (3) via hydrozine (2) proceeds smoothly at Hg, Cu and Pb cathodes in EtOH and MeOH, containing 5, 10, 15 or 20% HCl as supporting electrolyte.

In this reduction process organic substrate first appears to undergo protonation which is followed by one electron transfer forming the free radical R_2 N.NOH which immediately takes up three more pro-

0013 466 x (35) 36 203-204

TABLE 1

EFFECT OF CATHODE MATERIAL CURRENT = 0.3 Amp (c.d. = 0.0078 Amp/cm^2); ANODE = Pt FOIL ; ROOM TEMP = 25 ± 1°C

Cathode	Cell Voltage	Mass yield as hydrochloride %
Catholyte EtOH from containing 10 % HCl		
Hg	4-6	50.2
Cu	9-10	54.7
Pb	5	46.3
Catholyte MeOH containing 10 % HCl		
Hg	7	45
Cu	6-8	55.5
Pb	9-12	42.5

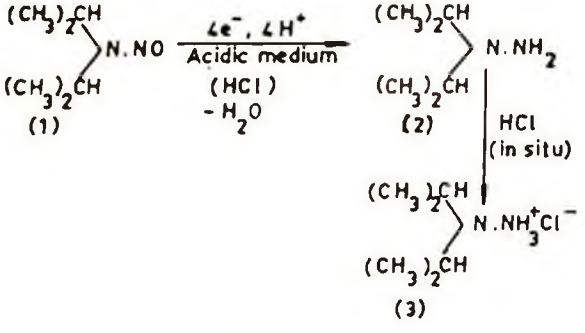


TABLE 2

EFFECT OF TEMPERATURE

Cathode Hg; current = 0.3 Amp (c.d.=0.0078 Amp/Cm^2); catholyte 10% HCl in EtOH (v/v)

Temp	% yield	Temp	% yield
10	47.5	15	50.5
20	50.5	25	50.0
30	49.5	35	49.0
40	47.2	45	39.3
50	38.0	55	35.5

tons and three electrons simultaneously forming the hydrazine. Tables (1-3) showed very well that the catholyte composition, the nature of the solvent, viz. EtOH and MeOH and also the nature of the cathode material do not play a very significant role in the reduction in acidic conditions, as the overall yields of product varies between 45 to 55% in each experiment. Of course, the temperature was found to affect the yield adversely above 40° C.

TABLE 3

EFFECT OF CATHOLYTE CONCENTRATE

Cathode = Hg; current = 0.3 Amp (c.d.= 0.0078 Amp/cm^2); Temp 25 ±1

% HCl in EtOH	5	10	15	20
% Yield	48	48.5	47.5	46

It may be because of the fact that at higher temperature hydrogen evolution becomes dominant.

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