

SYNTHESIS OF PREPARATIVE CONCENTRATIONS OF Nb(III) IN FORMAMIDE AND
DIMETHYLFORMAMIDE SOLUTIONS

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(Received 16 March 1972)

Besides the reduction of Nb(V) to lower oxidation states in superdry EtOH, we also studied the reduction in other non aqueous, well solvating electrolytes. This study has been performed in order to realise not only an optimum in the formation velocity of reduced Nb, but also in the reactivity of the solution after reduction.

Firstly we describe the behaviour in Formamide HCONH_2 and Dimethylformamide $\text{HCON}(\text{CH}_3)_2$ solutions. The reductions were carried out with the revised cell model II (1).

Both liquids being good electrolytic solvents and strong electron donors, we expected a more rapid reduction of Nb(V) in comparison with the EtOH/ NbCl_5 system. The preliminary results in Formamide underlined this hypothesis. Solution of NbCl_5 in formamide - faintly yellow - became black violet during reduction. This colour change proceeds more rapidly than in the EtOH system. In the same concentration range of Nb applied voltage and current density were comparable.

Note. Before electrolysis NbCl_5 was dissolved in (Dimethyl) formamide under dried, oxygen free N_2 -gas, the solution was filtered off, and a small amount of HCl-gas was introduced (see also 1).

Again the presence of HCl was necessary to favour the reduction process.

The percentages of reduced Nb - up to 15% - are small compared with those in EtOH, but on the same level as some syntheses of Nb(III), e.g. Nb_3Cl_8 at high temperature. Thus Teague et al. (2) obtained a 10% yield of Nb(III) product from the system Nb/excess PbCl_2 at temperatures between 550° and 800°C .

At prolonged electrolysis - more than 30 hours - the solution decolours, under formation of a precipitate. Analysis showed that at this instance no reduced Nb was left in the solution, all reduced Nb had disappeared in the precipitate. These phenomena were observed when HCl was still present, as a vivid evolution of H_2 -gas was perceivable at the cathode. Therefore in this procedure of synthesis, the upper limit of the percentage of reduced Nb is determined by the type of solvent in the system $\text{NbCl}_5/\text{Formamide}/\text{HCl}$.

The results in Dimethylformamide are inferior to those in Formamide. A first factor responsible for this result is the less pronounced solvolysis in DMF of NbCl_5 and so the evolution of wanted HCl, the main factor however is the small solubility - as observed - of additional HCl gas in DMF, being much lower than in FM. After prolonged electrolysis the same behaviour as for the Formamide solution is observed, i.e. decolouring of the solution and deposition of a precipitate.

Sherman and Archer (3) also obtained a precipitate after exhaustive electrolysis of a solution of NbCl_5 in DMF in polarographical concentrations; the product was white and insoluble. Under these circumstances the original solution consists of NbOCl_3 they suppose, as Golub and Sych (4,5) pointed out that the conversion of NbCl_5 to NbOCl_3 proceeded rapidly, due mainly to the presence of 1 m M residual H_2O in DMF. In our circumstances NbCl_5 is present in large excess - 0,25 M -, Moreover the solution is filtered off before electrolysis.

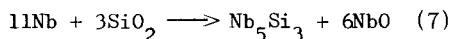
According to electrogravimetric analysis Sherman and Archer supposed the final product to be NbO. This seems doubtful however. The first precipitate in DMF is white, in FM sandcoloured. In both systems the colour of the deposition gradually darkens during continued precipitation.

Also the content of Nb rises in the course of precipitation; there is no uniform product. According to Hardy and Hulm (6) NbO is silver grey coloured and has a metal like appearance.

TABLE

	Colour	Nb	C	H	N	Cl
	DMF (begin) white	24,48	25,01	5,78	7,74	1,15
Precipitation	DMF (end) sand colour	38,08	12,06	3,72	12,93	negative
products	FM (begin) faintly yellow	24,65	17,81	4,62	18,65	< 0,20
	FM (end) light brown	38,12	8,95	3,59	9,86	< 0,20
(No direct Oxygen analysis)						

The final Nb percentages were obtained four days after the initial precipitation. Therefore a further increase in the percentage of Nb is unlikely. NbO however must contain 85,3% Nb. Also direct interaction between NbCl_5 in solution and the glass wall of the system causing formation of NbO is unlikely; only Nb (powder) reacts slowly with the glass wall in "dry systems" at 800°C .



Production of Nb(III) in higher percentages being not possible by direct electrolysis in FM and DMF, we obtained the wanted results in the following way however. First a solution of NbCl_5 in EtOH is electrolysed until a 100% reduction to Nb(III) has been obtained. Next the solution is repeatedly evaporated under N_2 (Ar) gas till a residual pressure of 0,05 mm Hg has been reached, each time followed by dissolving the residue in Formamide. The obtained solutions are stable under N_2 (Ar) gas atmosphere and are suitable for synthetic demands. The latter result shows that decomposition of Formamide (Dimethylformamide) is responsible for the described results of the system $\text{NbCl}_5/\text{FM}(\text{DMF})$ during the electrolytical reduction.

ACKNOWLEDGEMENT

Element analysis were carried out under supervision of W.J.Buis at the Micro-Analytical Department of the Institute for Organic Chemistry TNO, Utrecht, Netherlands.

The authors thank Dr.G.H.J.Broers for corrections.

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