

REDUCTION OF Nb(V) TO Nb(III) IN ETHANOL SOLUTIONS AND SYNTHESIS OF
Nb(III) TRILACTATE

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A Nb(III) compound was needed as starting material for the synthesis of several Nb(III) complexes.

The best known compound with this valence is NbCl_{3+x} (1) which is prepared by high temperature reactions, e.g. the oxidation of Nb with HCl, PbCl_2 etc, or the reduction of NbCl_5 with H_2 , Al, SnCl_2 etc. However these reactions lead to products with mixed valence state NbCl_y , with $2,72 < y < 3,13$. Generally the obtained product consists of a solid mixture of reactants and final product, separation being difficult. Furthermore, a high halogen concentration catalyses the formation of metal clusters such as Nb_3Cl_8 , the reactivity of such clusters is low. To find a better starting material we tried to reduce electrolytically solutions of NbCl_5 .

Most of the literature concerning this type of reduction deals with the polarographic reduction of NbCl_5 at a Hg cathode in concentrated HCl (10-13 M), Nb being present in only polarographically interesting concentrations (1-10 MF) (2,3,4,5). This information is not very useful for us for several reasons. For example, the reduction path depends already on the Nb concentration within the small polarographical concentration range, whereas we want to work with concentrations of about 0,5 M, in connection with synthetical demands. The high halogen concentration promotes the formation of clusters and the presence of H_2O may lead to oxobridged dimers. Because these species are unwanted, H_2O and HCl must be avoided in our experiments.

So we first tried to reduce NbCl_5 in superdry EtOH without any HCl being present.

However partial solvolysis of NbCl_5 brings some HCl into solution. The Nb(V) solution was neutralised by adding slightly more than 5 mole NaOEt per mole NbCl_5 . The solution was refluxed and NaCl deposited. Small quantities of HCl gas were introduced till no further deposition of NaCl occurred in order to remove the variable excess of NaOEt. Buslaev and Kokunov (6) showed that in 0,01 M NbCl_5 solution in ethanol $2,2 \pm 0,1$ of the 5 Cl had been substituted by the solvent, we found however that this substitution number rises with increasing Nb-concentration to a nearly complete substitution of chloride (4,85).

The quantity of HCl produced by solvolysis was measured with two titrations. One is used to determine the HCl escaped from the solution; this is captured in a know excess of NaOH. The second potentiometric titration with 0,02 M AgNO_3 in ethanol determines the HCl dissolved in EtOH. An Ag electrode is used versus S.C.E.

The NaCl was filtered off, some Nb-compound coprecipitated. In this way the solution was freed from HCl.

It was tried to reduce this solution under nitrogen atmosphere in two types of electrolytic cells, the first containing a carbon cathode, a sintered glass diaphragm and a mercury pool anode, the second was identical except for a carbon anode (Fig. 1,2,3). Under these conditions no reduction took place however. The introduction of a small amount of HCl gas started the reduction immediately, a brown-black or blue-black darkening of the solution was observed. During the reduction H_2 -gas was evolved. When this evolution stopped no further reduction occurred. On the contrary, the content of Nb (III) diminished with time, probably due to diffusion between the two compartments. Addition of more HCl gas restarted the reduction at once.

Thus having established the necessity of acid for a succesful reduction of Nb(V), we used the following procedure. Finely grinded NbCl_5 was dissolved under nitrogen gas in a small amount of ethanol, followed by dilution with more ethanol. In this way about half of the produced HCl escaped from the solution, the concentration of HCl varying as a function of the Nb-concentration between 0,3 and 1,5 M. The obtained solution was reduced in both electrolytic cells; 97% of the original Nb(V) could be reduced to Nb(III). The Nb(III) content

is measured by titration with excess I_2 in EtOH followed by back-titration with $Na_2S_2O_3$ in H_2O . The total amount of Nb is measured as Nb_2O_5 after filtration and glowing the residue at $1000^\circ C.$ [Ⓜ]) A direct-current power supply 0.35 V, 0-1 A was used for the electrolysis. The begin voltage of the carbon cathode versus S.C.E. was 1,25 to 2,25 V as function of the H^+ and Nb concentration, the initial current was about 100 mA. During the electrolysis the current gradually decreases; as soon as a constant value has been reached, the electrolysis is interrupted and the Nb(III) content is determined in the described way.

Cell I (fig. I and III), with a carbon cathode above a Hg anode, forms a Hg_2Cl_2 precipitate in the anodic compartment which effectively avoids the diffusion of the oxidated product to the cathode. With a slow rotating stirrer the Hg_2Cl_2 is wiped off the circular anodic surface and deposited in the side compartment. If necessary, fresh Hg can be supplied from time to time into the cylindric anodic vessel from a container via regulating stopcocks. A temporary rising of the anodic fluid level is compensated by means of an overflow to a little side container vessel. The rubber cork (fig. III) contains drilled holes for nitrogen gas in- and outlet, stirrer, electrode, salt bridge to S.C.E.

Cells II (fig. II and III) with two carbon electrodes is easier in operation. The anodic compartment is now above the cathode. It is flushed with nitrogen gas to remove the influence of evolved chlorine gas. The cathode compartment is stirred; three entries are present for the carbon cathode, nitrogen gas and salt bridge.

TRILACTATE

Earlier investigations showed that insufficient reduction or a high concentration of HCl in the solution yield to complex compositions of the products prepared from the Nb(III) solution. For that reason we report here the synthesis of the new compound Nb(III)-lactate: 10 ml. lactic acid is added slowly to 5 ml. Nb(III) solution (0,5 M) under N_2 -gas. Best results were obtained when after addition of the reagents a boundary layer was still perceivable between the reactants. After four days the solution becomes green. After ten days a yellow precipitate was formed. It was filtered off, washed several

times with superdry EtOH and dried in vacuo. Analysis percentages found (calculated): C 29,87 (30,01), H 4,30 (4,20), Nb 25,47 (25,79), Cl 0,47 (0,00); calculated on formula $\text{Nb}(\text{C}_3\text{H}_5\text{O}_3)_3$.

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

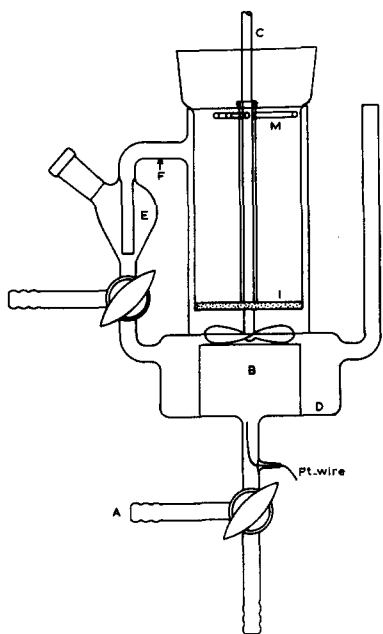


FIG. 1

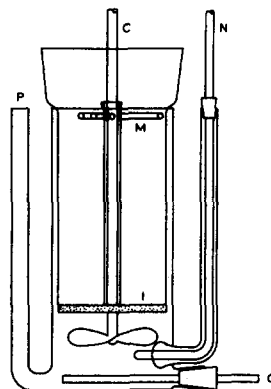


FIG. 2

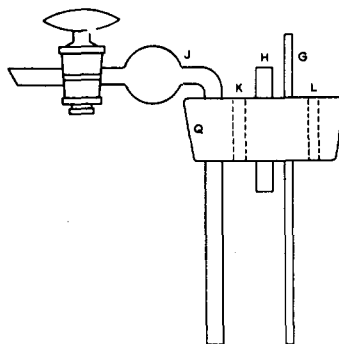


FIG. 3

A connection to Hg supply vessel B cylindric glass filled up with Hg C stirrer D side compartment E overflow F electrolyte level G carbon electrode H glass bearing I sintered glass diaphragm J nitrogen gas entry K, L nitrogen gas outlet, salt bridge M bearing supporting rods N nitrogen gas entry (polyethene tube) O carbon electrode P salt bridge entry Q rubber cork. Total electrolyte about 200 ml.

In order to allow a complete deposition of the Nb compound, the solution is heated before filtration.

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