

makes their experimental evaluation impossible. On the other hand, the acid strengths of the hydrogens in question cannot be a limiting factor; for less acidic compounds more basic media can be used in the kinetic measurements involved.

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1. Salomaa, P. and Sallinen, K. *Acta Chem. Scand.* 19 (1965) 1054.
2. The computer program was written in this laboratory by Mr. M. Hotokka, B.Sc.

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Electrolytic Nitrogen Fixation in a Molten Salt

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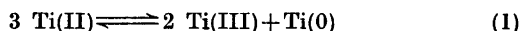
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Electrolytic reduction of nitrogen in the presence of transition metal complexes has recently been reported.^{1,2} In the most successful version, a solution of titanium tetraisopropoxide, aluminium isopropoxide, naphthalene and tetrabutylammoniumchloride in 1,2-dimethoxyethane was electrolysed under an atmosphere of nitrogen. Up to 6.1 mol NH₃ was produced per mol titanium.^{1b}

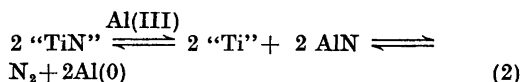
In the early electrolytic experiments it was evident that the solvent (tetrahydrofuran, THF) was partially decomposed, giving tarry deposits on the electrodes. In addition to being ideal solvents for electrolytic reactions, molten salts should generally be more stable than most organic solvents. We have therefore investigated the electrolytic reduction of molecular nitrogen in a molten mixture of aluminium chloride, potassium chloride, and sodium chloride containing titanium chloride. Quantitative data from two representative experiments are given in Table 1.

The electrolysis cell was equipped with a platinum cathode and an aluminium anode. In order to avoid chemical reduction by aluminium metal (*cf.* Ref. 3) the electrode compartments were separated by two consecutive glass filters. During electrolysis,

approximately the required amount of aluminium was dissolved at the anode (Table 1). No chlorine was evolved. When molecular nitrogen was bubbled through the cell during the electrolysis, reduction occurred as evidenced by the formation of ammonia on hydrolysis of the electrolyte. No ammonia was detected if the electrolysis was performed under helium or if titanium tetrachloride was omitted. Hydrazine could not be detected by qualitative tests. Reduction of molecular nitrogen to the ammonia stage started when approximately 2 F per mol of titanium had been passed through the cell. This is in accordance with van Tamelen's suggestion that titanium(II) is the active catalytic species.⁴ A maximum yield of ammonia (0.25 mol/mol Ti) was obtained at 4–6 F per mol titanium, then the yield decreased slowly. Electrolytic deposition of titanium on the cathode is insufficient to explain the relatively low maximum yield. A possible explanation for the observed maximum yield of ammonia is that titanium metal separates from the molten phase due to the equilibrium (1) which is strongly displaced towards Ti(0).⁵



Another possible but hypothetical explanation is that the reduced titanium-nitrogen species is in equilibrium with molecular nitrogen according to eqn. (2). The existence



of such an equilibrium is indicated by a rough calculation using Volpin's data on the titanium catalysed reduction of molecular nitrogen by aluminium metal in molten aluminium bromide³ (see Table 2). Reduction of nitrogen to ammonia and of titanium(IV) to titanium(0) does not account for all the current consumed. A reasonable explanation would be cathodic reduction of aluminium(III). However, no aluminium was deposited on the cathode during the electrolysis.

Table 1. Experimental data.

Exp. No.	TiCl ₄ mmol	Current mF	NH ₃ found after hydrolysis, mmol	Current yield for the oxidation of Al at the anode %
1	19	131	4.6	82
2	21	274	4.1	75

Table 2. Nitrogen reduction in the system $\text{TiCl}_4\text{--Al--AlBr}_3$. Data from Ref. 3.

$\text{TiCl}_4\text{:Al:AlBr}_3$	$\text{NH}_3/\text{TiCl}_4$	Mol fractions of AlN	Al^{3+}	N^{3-}	Activity of AlN
1:12:16	6.44	0.286	0.960	0.110	0.106
1:12:33	10.7	0.236	0.979	0.0943	0.092
1:150:200	95	0.320	0.995	0.136	0.135
1:600:1000	284	0.221	1.00	0.0864	0.087

In conclusion, titanium catalysed electrolytic reduction of molecular nitrogen is possible in a molten salt. The reduction is inefficient, probably due to precipitation of titanium metal according to eqn. (1). Other catalysts should therefore be investigated.

Experimental. The electrolysis cell consisted of a 100 ml four-necked flask into which a filtering tube with a ground glass joint could be fitted. This tube served as anode chamber. The anode was a sheet of aluminium which dissolved during the electrolysis (anodes of platinum and carbon were found to disintegrate rapidly during the electrolysis). The cathode was a sheet of platinum and the current was supplied by a stabilized DC-power supply. All chemicals used were dry and free from ammonia as determined with Nessler's reagent.

The eutectic mixture (about 150 g) of AlCl_3 (63.5 mol %), KCl (16.5 mol %), and NaCl (20.0 mol %), m.p. 89°C was placed in the reaction flask which was heated to 100°C in a thermostated oil bath. Titanium (IV) chloride was added and the electrolysis started. The current was kept at 0.25 A. An atmosphere of nitrogen was maintained in the flask during these operations. At intervals, samples were taken and analysed for ammonia with Nessler's reagent. Tests for hydrazine in the melt were negative. After the electrolysis, the total amount of reduced nitrogen was determined as ammonia by Kjeldahl analysis. Maximum yields of about 0.25 mol NH_3 /mol Ti were obtained at 4–6 F/mol Ti. If the electrode compartments were not rigorously separated, up to 1.5 mol NH_3 /mol Ti were obtained, probably due to reduction by aluminium metal.

During the electrolysis, small amounts of titanium were deposited on the cathode, as indicated by an analysis of the surface of the cathode (0.00 % Al, 3.24 % Ti) (a few mg of the outer surface were removed by scraping).

In the calculation using Volpin's data the mol fractions of aluminium ions and nitride ions in the melt were calculated from the reported compositions of the melt and the reported yields of ammonia. The activity of aluminium nitride was then taken as the product of these two mol fractions.⁷ This product was roughly constant as required by eqn. (2) at a constant nitrogen pressure.

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