its progenitors was further confirmed by thin layer chromatography and by the appearance of a blue color with Ehrlich's reagent within a few minutes of dissolution of the adduct.[11] It was possible to obtain uv and ir data for **6** and these support the Diels–Alder structure.

---

(11) In contrast, isoindole 2 reacts at once with Ehrlich's reagent. (Compound 2 also gives an immediate deep violet color in the pine splint test.)

Joan E. Shields
Department of Chemistry, C. W. Post College
Brookville, New York 11548

Joseph Bornstein
Department of Chemistry, Boston College
Chestnut Hill, Massachusetts 02167

Received June 20, 1969

The Catalytic Fixation of Molecular Nitrogen by Electrolytic and Chemical Reduction

Sir:

For some years this laboratory has been investigating the chemical modification of molecular nitrogen under mild conditions, by means of experiments based on the concept of titanium(II) as the fixing species.[1–5] We now wish to report the innovation of an electrochemical system in which titanium *catalytically* effects reduction of nitrogen to the ammonia level.

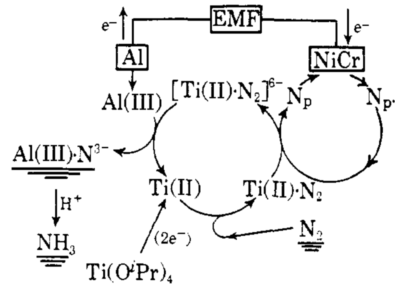
In the most successful experimental variation,[6] the electrolysis cell was fitted with an aluminum anode and a nichrome cathode, and contained a 60-ml 1,2-dimethoxyethane (glyme) solution of 1.68 mmol of titanium tetraisopropoxide, 7.6 mmol of naphthalene, 8.6 mmol of tetrabutylammonium chloride, and 42 mmol of aluminum isopropoxide. The solution, while being stirred under a slow stream of pure nitrogen, was electrolyzed at 40 V until the conductance of the cell had greatly diminished (11 days); during this time 0.155 faradays had passed through the cell and 15.1 mmol of aluminum had been lost from the anode. When the solution was treated with 40 ml of 8 *M* aqueous sodium hydroxide solution and heated in a water bath, the product ammonia (10.2 mmol, 610% yield, based on NH_3:Ti molar ratio) could be blown into an aqueous hydrochloric acid trap by a stream of gas.

When titanium tetraisopropoxide was omitted or when argon was substituted for nitrogen, no ammonia could be detected. In the absence of naphthalene, ammonia was formed, but in decreased yield. Apparently, the naphthalene functions primarily as an electron carrier, being reduced to naphthalide by the cathode and oxidized back to naphthalene by titanium–nitrogen species. Indications of the presence of naphthalide are: (1) attack of the Teflon-coated stirring bar (a property of sodium naphthalide and some other strong reducing agents) only when naphthalene is included, and (2) when the titanium tetraisopropoxide is omitted, generation of a dark greenish brown substance (sodium naphthalide in glyme is an intense brownish green) at the cathode.[7] It should be noted that naphthalide does not react with aluminum isopropoxide in glyme, as determined in a separate series of experiments.

We conjecture that the aluminum isopropoxide, in addition to serving as an electrolyte, frees the lower valent titanium compound of reduced nitrogen so that it can fix more molecular nitrogen.[8] In keeping with this hypothesis is the observation that, in a single cycle, the chemical fixation–reduction of nitrogen becomes catalytic with respect to titanium (275% NH_3) when aluminum isopropoxide is included in the previously reported[2,3] reaction of sodium metal with a glyme solution of naphthalene and titanium tetraisopropoxide.

Our observations to date are consistent with the reaction sequences diagrammed in Chart I. The electrolytic reduction of nitrogen and aspects of related titanium–aluminum systems are under continuing investigation at this time.

Chart I[a]



[a] Lower valent titanium may be monomeric or polymeric.

Acknowledgment. Financial support was provided by the National Institutes of Health (Grant GM 13797).

---

(1) E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.*, **87**, 3277 (1965).

(2) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *ibid.*, **89**, 5707 (1967).

(3) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).

(4) E. E. van Tamelen and B. Åkermark, *ibid.*, **90**, 4492 (1968).

(5) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *ibid.*, **91**, 1551 (1969).

(6) Yields varied between 257 and 610%.

(7) Apparently the naphthalide is oxidized by tetrabutylammonium ion in the absence of titanium tetraisopropoxide and not by the anode since the dissolution of aluminum accounts for 99% of the electrons recovered from the anode. Tributylamine can be recovered from the reaction mixture after work-up (82%). However, it is clear that the tetrabutylammonium chloride is being slowly consumed in some way, since the conductivity of an electrolysis solution after prolonged electrolysis is a fraction of its initial value and can be restored by addition of more tetrabutylammonium chloride. When sodium naphthalide is allowed to react with tetrabutylammonium chloride under a stream of nitrogen, tributylamine is found in the reaction flask and 1,2-dibromobutane is found in a dilute bromine solution through which the effluent gas is passed.

(8) *Cf.* M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *Chem. Commun.*, 1074 (1968).

(9) National Institutes of Health Postdoctoral Fellow, 1969–.

Eugene E. van Tamelen, Douglas A. Seeley[9]
Department of Chemistry, Stanford University
Stanford, California 94305

Received July 19, 1969

Photochemistry without Light

Sir:

We wish to report a general method for achieving "photochemistry without light."[1] The principle in-

---

(1) This expression has been used previously in a specific case where it was suggested that a common intermediate might have been involved in a photochemical and a nonphotochemical reaction: H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969).