

Design and Development of an Organic-Inorganic System for the Chemical Modification of Molecular Nitrogen under Mild Conditions

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Received June 24, 1970

Two important modes of molecular nitrogen (N_2) fixation are well recognized: the biological conversion of aerial N_2 to the NH_3 level, and the catalyzed synthesis of NH_3 from N_2 and H_2 at high pressures and temperatures (Haber process). Although its operation on Earth has long been apparent, the mechanism of the biological process for years has remained veiled from the eyes of the scientific observer, and only recently have some chemical insights been gained into this natural phenomenon.

Just as the enzymic N_2 -fixation process is indispensable in a chemically balanced planet, so is the Haber process an integral part of our chemical industrial complex. Invented less than a century ago, the Haber operation has dominated the NH_3 scene and has remained through the years, in essentially unmodified form, as the most efficient and inexpensive method for NH_3 synthesis on the industrial scale.

Why, then, the interest in developing and studying new methods for the fixation and chemical transformation of N_2 ? In regard to the biological phenomenon, it seems probable that the chemist, with his particular viewpoint and methodology, will contribute significantly to our understanding here, just as he has in other areas of biology. In terms of industrial development, the Haber process will probably not be displaced as long as H_2 remains cheap. On the other hand, the Haber method, by definition, is restricted to the manufacture of NH_3 and no other product. Also, with the eventual decline of the internal combustion engine and concurrent decrease in gasoline production, by-production of H_2 in the petroleum cracking process will fall off, and other sources of this raw material may have to be sought.

In the decades to come, it is possible, then, that there may emerge new industrial methods for utilization of N_2 , involving either alternative methods for NH_3 synthesis or the direct production of useful compounds

other than ammonia. Partly because of these reasons, but mostly because of an interest in the purely scientific aspects, we addressed ourselves during the 1960's to the problem of discovering new methods for the chemical transformation of N_2 , especially such methods as would operate under the mild conditions of atmospheric pressure and room temperature.

Despite the absence of prior practical or theoretical knowledge bearing on the issue, the prospects of fixing, and possibly otherwise chemically modifying, N_2 under mild conditions seemed good, if only because nature had already demonstrated that such chemistry was possible in living systems. Although having the advantage of enzymic assistance, nature is restricted in its operations by being required to operate in essentially aqueous media, at a pH close to 7, at ambient temperatures, and with chemical agents compatible with other cellular materials. On the other hand, in the nonenzymic laboratory, such stringent requirements do not exist, and the basic N_2 chemistry might be executed, *e.g.*, in non-aqueous solvents, under widely varying pH conditions, or with fixing species intolerable to the living system. Thus, this research project, like counterparts in the organic natural product synthesis area, can be looked upon as an exercise in "biogenetic-type" synthesis!¹

Design

At the time the above point of view was being entertained, transition metal agents (specifically, iron porphyrins) were already implicated in the biological fixation process. Also, in the early 1960's, we happened to have been engaged in work on the chemistry of diimine (H_2N_2) and were aware of the considerable catalytic effect of Cu(II) in the reduction of azobenzene (but not of olefins²), behavior indicating the ability of a transi-

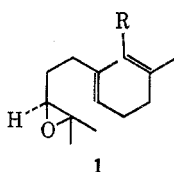
(1) E. E. van Tamelen, *Fortschr. Chem. Org. Naturst.*, **19**, 242 (1961).

(2) Unpublished observations, R. S. Dewey and R. Lawton, University of Wisconsin, 1961. Attempts in 1961 to observe the conversion of N_2H_2 (from azodicarboxylic acid) to NH_3 by a leguminous system were unrewarding (E. E. van Tamelen and R. Burris). For a review of diimine chemistry, see S. Hunig, *Angew. Chem.*, 368 (1965).

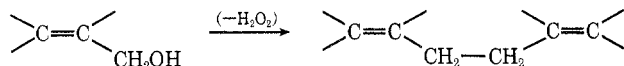
† Recipient of the 1970 American Chemical Society Award for Creative Work in Synthetic Organic Chemistry, sponsored by Synthetic Organic Chemical Manufacturers Association.

tion metal to coordinate effectively with N≡N bonds. In view of the latter phenomenon, it seemed possible that Cu(I), for example, might fix N₂ while forming a Cu(II)-diimine complex, which itself might be further chemically modified. Attempts by Dr. Alexander H. Todd and Mary F. Lease during these early years to capitalize on the above notions were made, the fixation experiments featuring as potential agents Cu(I)/Cu(II) and also transition metal complexes of tetramethyl-hematoporphyrin.

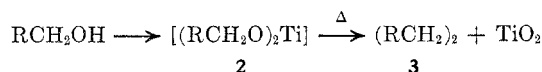
Concurrently, a new lead to the N₂-fixation goal opened up in our laboratories by reason of research activity in a distinctly different area. Bioorganic investigations involving preparation and study of terpenoid terminal epoxides (**1**)³ called for a method of reductively coupling alcohols, at the time an unknown reaction type.



One plan, ultimately reduced to practice in 1965,⁴ depended on the anticipated behavior of the dialkoxide of a metal in a lower valent (II) state, less stable than

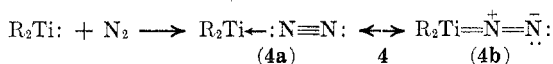


the higher valent (IV) level. Titanium was selected as the inorganic performer, and the successful reaction featured *in situ* generation of titanium(II) alkoxide (**2**)



by one of several means, followed by thermally induced extrusion of TiO₂ and formation of the coupling product (**3**) under mild conditions (<100°). Actually proved only later to involve titanium(II) intermediates,⁵ the reaction based on the above concept made available at this early time species believed to be titanium dialkoxides (**2**).

Being in a formal sense titanium analogs of a carbene and undoubtedly possessed of considerable reduction and coordination power, monomeric titanium(II) species seemed likely candidates for direct reaction with molecules of low nucleophilic power, such as N₂. Following the crude carbene analogy one step farther, one might imagine formation of an adduct (**4**) in which the



bound N₂ unit has lost the electronic character of the N₂ molecule (**4a**) and the electronic contribution of the "diazo" canonical form (**4b**) would be sufficient to per-

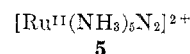
(3) E. E. van Tamelen, *Accounts Chem. Res.*, **1**, 111 (1968).

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

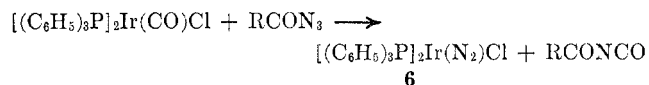
(5) E. E. van Tamelen, B. Åkermark, and K. B. Sharpless, *ibid.*, **91**, 1552 (1969).

mit further reaction of the N₂ unit—specifically, reductive cleavage of the nitrogen–nitrogen bond as well as the titanium–nitrogen bond, with resultant formation of two NH₃ molecules for each N₂ unit. With the above possibilities in mind and specifically basing the design of experiments on the titanium(II) concept,^{4–6} we initiated N₂ fixation research in the mid 1960's

Also at this time, significant findings in the nitrogen fixation area were made in other laboratories. Vol'pin and coworkers reported that varying amounts of NH₃ are formed after protonation of a reaction mixture resulting from the action on N₂ of a mixture of a transition metal compound with a hydrogen source such as a metal hydride or Grignard reagent.⁷ Later, Allen and Senoff, in attempting to prepare ammine complexes of ruthenium by reaction of hydrazine hydrate with RuCl₃, discovered the first stable transition metal system bearing a N₂ ligand, nitrogenpentaammineruthenium(II) (**5**).⁸



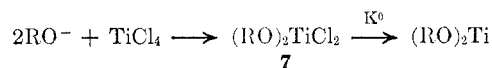
Shortly thereafter, Collman and Kang then recognized that the product of the reaction between Vaska's compound and an acyl azide is not the iridium(I) species with the RCON ligand but rather the N₂ ligand case **6**, formed with loss of acyl isocyanate.⁹ In 1967, forma-



tion of specifically identified nitrogen transition metal compounds by direct reaction with N₂ was reported by several groups,¹⁰ including the remarkable generation of Allen and Senoff's ion in aqueous solution, observed by Harrison and Taube.¹¹

Development

In our earliest successful experiments, begun by Dr. S. Ela, a titanium(II) alkoxide was generated by the same method used in the coupling reaction, *vis.*, potassium metal induced dehalogenation of Ti^{IV}Cl₂(OR)₂ (**7**), in



turn prepared directly from TiCl₄ and alkoxide ion.⁶ In a typical case, TiCl₄ (1.0 mole equiv) was added to a suspension of potassium *tert*-butoxide (2.0 mole equiv) in diglyme at 0° under an atmosphere of nitrogen. The suspension of dialkoxytitanium dichloride was allowed to warm to room temperature, and potassium metal (2.0 equiv) was added. Reduction of the Ti(IV)

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

(7) M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966), and references cited therein.

(8) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

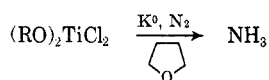
(9) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **88**, 3459 (1966).

(10) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); A. Sacco and M. Rossi, *ibid.*, 316 (1967); A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Jap.*, **40**, 700 (1967); see also A. B. Shilov, A. K. Shilova, and Y. G. Borodko, *Kinet. Katal.*, **7**, 768 (1966).

(11) D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 5706 (1967).

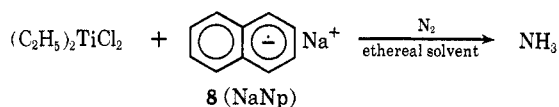
species was evident by the change in color from off-white to black and by the disappearance of potassium metal within 12–24 hr. Throughout these operations, purified nitrogen was allowed to bubble through the reaction mixture and into a trap that contained a dilute aqueous solution of either boric or sulfuric acid. Under these conditions, direct ammonia production continued for at least several weeks. When the reduction of titanium(IV) was carried out in a stepwise manner, ammonia was not generated after the first equivalent of potassium had been consumed, but only after the second equivalent had been added. Ammonium ion was also detected when reaction mixtures were subjected to hydrolysis with acid.

On the basis of various observations, we regarded ethereal solvent as the most likely source of hydrogen in the process leading to volatile ammonia. Later, by employing perdeuteriotetrahydrofuran as solvent and running mass spectral determinations on volatile ammo-



nia formed, this surmise was confirmed.¹²

At this same time Dr. G. Boche made in our laboratory a noteworthy discovery, referred to briefly in our preliminary publication.⁶ Again, in an experiment designed to involve a Ti(II) species—in this case, “titanocene” (Cp_2Ti)₂[−],¹³ the first observation of fixation of N₂ by a cyclopentadienyltitanium–naphthalene radical-anion (NaNp) system (**8**) was made. This system was destined to provide the key for mechanistic understand-



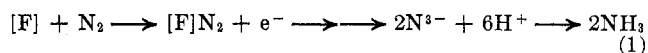
ing of the titanium-promoted fixation reaction, taken up below.

As our experience in this titanium series broadened, a satisfactory, reasonably efficient N₂ fixation reaction emerged. In an exemplary run, the reaction was carried out in a closed system under an atmosphere of pure dry N₂, with means for measuring volume changes. A solution of NaNp in tetrahydrofuran (THF), on being stirred rapidly during the addition of $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, absorbed N₂ at room temperature over a period of ~60 min.¹⁴ Upon addition of a proton source, as much as a 65% yield of NH₃ (based on the equation $\text{N}_2 \rightarrow 2\text{NH}_3$) was liberated.

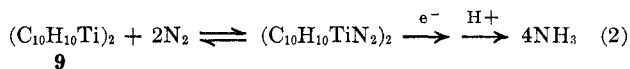
Mechanism

Just as separation of the oxidation and cyclization steps in the enzymic conversion of squalene to lanosterol was of fundamental importance and utility in the study of sterol biosynthesis,⁹ so was delineation of the complexation and reduction steps of basic value in

understanding the transition metal effected overall conversion of N₂ to NH₃. Experiments¹² with “titanocene” revealed that the fixation process is not a nondissectible merger of chemical phenomena, but rather a rational, sequential process of the general type 1, where [F] is a coordinating agent.



In a typical experiment dicyclopentadienyltitanium dimer (**9**) (“titanocene”), dissolved in anhydrous, oxygen-free benzene at 20–25°, was exposed with stirring to an atmosphere of N₂. During the course of approximately 3 weeks, >0.9 mole of the gas was absorbed, after which uptake ceased. Similar behavior was observed when a preparation of titanium(II) *n*-hexoxide (prepared by reaction of titanium(III) chloride, *n*-hexyl alcohol, and methyl lithium in a 1:2:3 molar ratio) was dissolved in benzene and exposed to an atmosphere of N₂. Significantly, titanium(II) allyloxide and benzyl-oxide, useful for achieving coupling of hydrocarbon units, were ineffectual in fixing nitrogen, possibly because of stabilization due to internal coordination with titanium of the π electrons of the unsaturated ligands. The titanocene–N₂ reaction is reversible under the con-



ditions described. Thus, in one run, the reaction was interrupted after 30% reaction by quickly flushing argon through the system; during the following 50 hr all of the chemically bound N₂ was released into the argon atmosphere, as indicated by the volume change.

Treatments of this titanium–nitrogen complex in benzene with excess NaNp and subsequent hydrolysis produced ammonia in quantitative yields. Further, a solution of this complex in benzene showed an infrared absorption at ~1960 cm^{−1} which may be attributable to an N–N stretch and which disappeared after the solution was exposed overnight to an argon atmosphere. An osmometric molecular weight determination in benzene indicated that the nitrogen complex is dimeric.

It is important at this point to note that, despite earlier claims,^{8,15} in the past no discrete transition metal compound with an N₂ ligand could be made to suffer reduction or oxidation of that affixed unit,¹⁶ seemingly, an order of stability sufficient to permit isolation of the N₂ ligand type also precluded chemical transformation of the ligand. In the examples of such cases which have been subjected to X-ray structural determination, it has turned out that the N₂ ligand is bound by the lone pair to the metal nucleus (**10a**).^{17,18} It thus appears that in an electronic sense the N₂ ligand is equivalent to the free N₂ molecule (**10a**) and is as refractory as the latter. In our Ti(II) species, the N₂ ligand is readily susceptible to complete reduction, suggesting, as does

(15) A. D. Allen and F. Bottomley, *Accounts Chem. Res.*, **1**, 360 (1968).

(16) J. Chatt, R. C. Richards, J. E. Ferguson, and J. L. Love, *Chem. Commun.*, 1522 (1968).

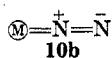
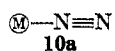
(17) F. Bottomley and S. C. Nyberg, *ibid.*, 897 (1966).

(18) J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *ibid.*, 96 (1968).

(12) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969).

(13) G. W. Watt, L. J. Baye, and F. O. Drummond, *ibid.*, **88**, 1138 (1966).

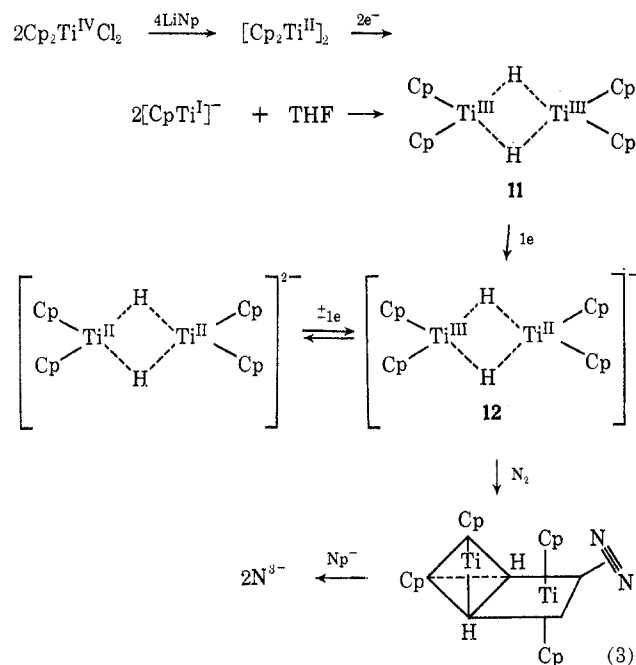
(14) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).



the low N–N stretching frequency, considerable double bond character in the ligand (**10b**). In any case, the titanocene–N₂ chemistry represents the first example of the specific preparation and subsequent reductive conversion to NH₃ of a transition metal compound made directly by reaction with N₂ or by other means (eq 2).

In order to ascertain the overall stoichiometry of the N₂-reducing reaction involving titanium, a Job plot was constructed in which the yield of ammonia was measured as a function of the starting titanium(IV) isopropoxide:sodium naphthalide ratio. The absence of either reagent precluded ammonia formation, while a maximum yield of product was observed at ~1:5–6, reflecting the redox relationship required for the overall conversion of N₂ to ammonia. Independently of the Ti:NaNp molar ratio, there was formed *approximately* 2 moles of ammonia per mole of N₂ taken up.

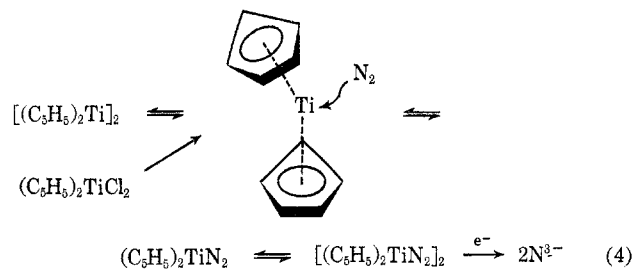
Subsequent to the appearance of our titanocene observations and mechanistic suggestions, Henrici-Olivé and Olivé submitted a manuscript featuring a distinctly different scheme (eq 3) for the fixation reaction, based largely on esr studies carried out on Cp₂TiCl₂–LiNp *in the absence of N₂*.¹⁹



Various experimental results indicate that this interpretation is untenable, and at the same time support, and permit elaboration of, our original proposal of eq 2^{6,12} (unpublished results, D. Seeley, S. Schneller, H. Rudler, and W. Cretney). (1) A distinct feature of eq 3 is the stoichiometric abstraction of protonic hydrogen from solvent THF by Cp₂Ti^I– to give presumably THF anion and the hydrogen-bridged dimer of Cp₂TiH (**12**), the precursor of the nitrogen-fixing species. We have found that treatment with T₂O of a titanocene–N₂-fixation reaction product does not lead to any isotopic label-

ing of THF solvent, thereby indicating that no THF anion is present at the end of the fixation–reduction process. Further, by glpc criteria, no new products are formed in significant amount from THF solvent, and thus neither THF α radical nor carbonium ion is apparently formed by hydrogen loss from solvent. (2) Although titanocene dimer is quantitatively converted by means of a reversible reaction in benzene to the titanocene·N₂ dimer,¹² no N₂ is observably fixed by a reaction mixture prepared by treatment of titanocene dimer in THF with 3.0 equiv of sodium naphthalide, as would be expected on the basis of eq 3. (3) Equation 3 demands a maximum NH₃ yield of 1.0 per titanium center, and there was observed a value of 0.96 in a 16-hr reaction carried out in THF under 1 atm of N₂ with Li:Ti = 6. Starting with the titanocene·N₂ compound, we have obtained in a more rapid reaction 2.0 moles of NH₃ per titanium, a result in keeping with eq 2. (4) In the case of both titanocene and titanium alkoxide N₂ fixation, the overall reaction proceeds much more slowly when the Ti(II) species is initially prepared under argon and used subsequently for the N₂ reaction than when it is prepared and used, *in statu nascendi*, under N₂. Such results are consonant with generation of a highly reactive Ti(II) monomer, which rapidly fixes N₂ when available, but which, in the absence of N₂, is converted to Ti(II) polymer, an inefficient source of monomer in an equilibrium situation.²⁰

Although the above body of results negates eq 3 as a *major* N₂ fixation pathway, reaction by a hydrogen abstraction route in a *slow*, low NH₃ yield, process remains possible, as demonstrated early in our laboratory (*vide supra*). It seems quite likely that the sensitive esr methods employed in the development of eq 2 reveal minor constituents of a complex reaction mixture and have little to do with the *major*, *rapid* fixation process. In light of the foregoing, original eq 2 can be accepted and expanded to eq 4.²⁰



An independent set of observations also supports the proposal that another Ti(II) species, Ti(OR)₂, is operative in the N₂ fixation chemistry utilizing Ti(OR)₄ or Ti(OR)₂Cl₂ as the starting material. Studies of the coupling reaction (*vide supra*) showed, for example, that a maximum yield of coupled product is realized when there is utilized such a number of equivalents of reducing agent as to reduce Ti(III) or Ti(IV) to the Ti(II) level—use of a greater or lesser amount of reducing

(20) The carbene-like character of monomeric titanocene has been supported by Hückel calculations: H. H. Brintzinger and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 1105 (1970). In the pictorial presentation of titanocene monomer, the structure featuring noncoplanar C₅H₅ units, suggested by these calculations, is used.

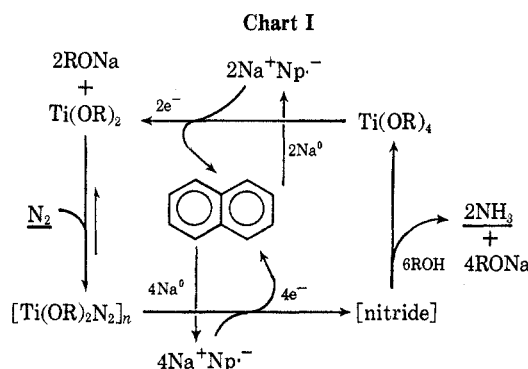
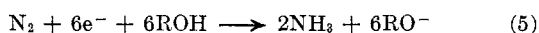
(19) G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **81**, 679 (1969).

agent greatly diminishes the yield. Also, it was possible to isolate, after reduction of $\text{Ti}(\text{OCH}_2\text{C}_6\text{H}_5)_2\text{Cl}_2$, a highly reactive substance which analyzed correctly for $\text{Ti}(\text{OCH}_2\text{C}_6\text{H}_5)_2$ and which gave a good yield of bibenzyl on pyrolysis under the conditions normally used in the overall coupling reaction.

The chemical circumstances of these coupling reaction observations are also those which obtain in the N_2 -fixation reaction, thus implicating $\text{Ti}(\text{OR})_2$ in the latter phenomenon as well. In the titanium alkoxide series, no reaction with N_2 is observed in systems (chemical or electrolytic) where $\text{Ti}(\text{III})$ is generated. Likewise, Ti^0 is evidently not a dominant fixing species in our system. If $\text{Ti}(\text{OR})_4$, in THF solution and under argon, is subjected to 4 equiv of NaNp for ~ 30 min—and thereby given ample opportunity to undergo over-reduction (observed), past the II level and to the zero state—and the argon then replaced by N_2 while additional NaNp is added, only minor fixation ($\sim 10\%$) takes place (unpublished results, S. Schnell). Although Olivé and Olivé report good evidence that N_2 -fixation reactions utilizing VCl_3 - LiNp and CrCl_3 - NaNp involve V^0 and Cr^0 , no such evidence was reported for the titanium series. Finally, the product of our fixation reaction is not titanium nitride but a complex, very reactive, petroleum ether soluble material which analyzed approximately as $\text{Na}_{13}\text{Ti}_3\text{N}_4(\text{OC}_3\text{H}_7)_{10}$ (unpublished results, R. Greeley), again suggesting that titanium alkoxide is directly involved in the fixation process.

A Fixation Cycle

An unpredicted but welcome extrapolation of the above chemistry was its development into an overall catalytic method for the conversion of N_2 into NH_3 at room temperature and atmospheric pressure, the first such cycle to be realized with transition metal species in solution.¹⁴ The basic reaction used in this application is the fixation brought about by NaNp and titanium isopropoxide, described above. Operation of a cyclic process depends on a sequence involving (1) judicious addition of the proton source isopropyl alcohol after N_2 absorption is complete and removal of volatile product NH_3 , and (2) addition of either additional NaNp or Na to regenerate the radical anion from naphthalene freed in the N_2 reduction stage, and attendant regeneration of the titanium species needed for further fixation. By such means, in excess of 170% yield of NH_3 was synthesized during the course of five cycles, making the process catalytic, in a net, overall sense. On the basis of the evidence accumulated thus far, we believe the pathway in Chart I represents the cycle by which N_2 is converted to ammonia in our system. Cyclical operation thus depends on the N_2 -fixing ability of titanium(II) as well as regenerability of titanium(II) and reduction of the titanium-bound N_2 , both brought about by NaNp available from a naphthalene pool by periodic reaction with reagent sodium metal. The overall net process is



It is evident that this mode of N_2 fixation differs from the original Vol'pin reaction⁷ wherein transition metal compounds are used in conjunction with alkyl Grignard reagents or metal hydrides as reducing species and hydrogen sources.²¹ Also, this cycle serves as a crude parallel or model for the biological N_2 -fixation process, which in its simplest form is thought to involve initial interaction of lower valent transition metal with N_2 from the air, followed by reduction of the coordinated N_2 species. In closer analogy with the biological process, extensive N_2 binding is observed when $\text{Fe}(\text{acac})_3$ is substituted for titanium(IV) in the transition metal- NaNp system (unpublished results, Dr. S. Schnell).

Electrolytic Fixation

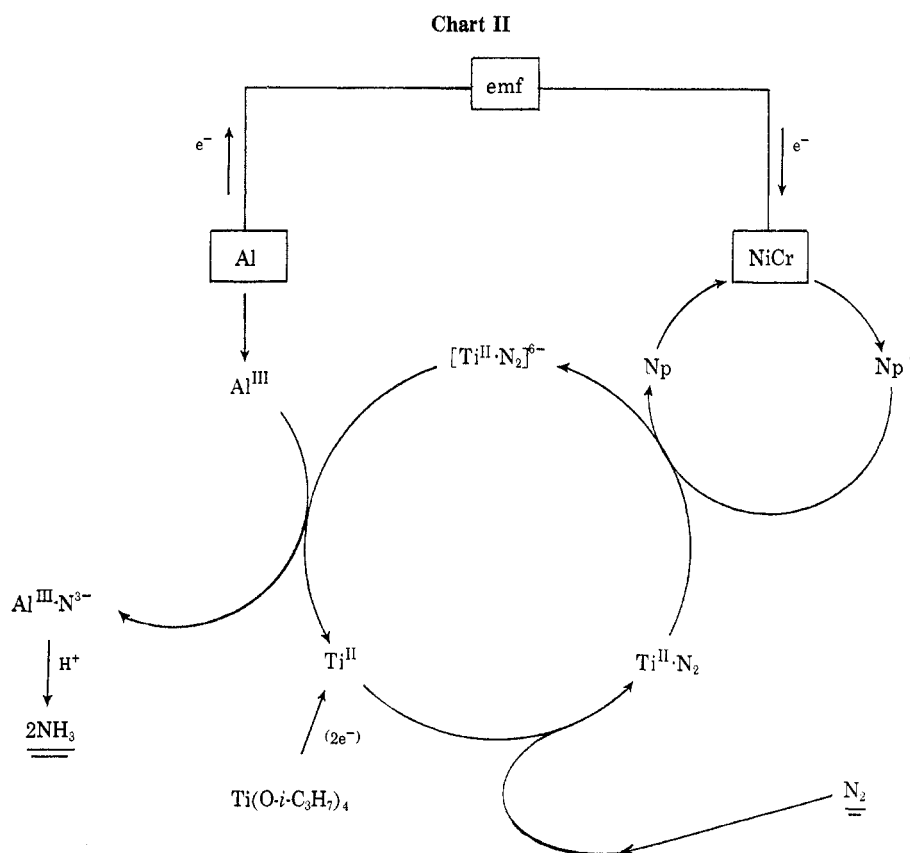
Mindful of the value in uncovering more practical electron sources than alkali naphthalides, we turned our attention to electrolysis. In preliminary experiments, the first significant reduction of N_2 to NH_3 was observed in a room temperature-atmospheric pressure procedure involving electrolysis with platinum electrodes of a titanium isopropoxide and AlCl_3 solution under N_2 .²² Later, as a consequence of certain improvements, the titanium-based *catalytic* electrochemical conversion of N_2 to NH_3 was developed, again achieved under mild conditions.²³

To an electrolysis cell, fitted with an aluminum anode and a nichrome cathode, was added a 1,2-dimethoxyethane (glyme) solution of titanium tetraisopropoxide, naphthalene, tetrabutylammonium chloride, and 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). When the solution was treated with alkali and heated in a water bath, the product ammonia was liberated in 150–300% yield. In the absence of naphthalene, ammonia was formed, but in decreased yield. The naphthalene functions primarily as an electron carrier, being reduced to naphthalide by the cathode and oxidized back to naphthalene by titanium nitrogen species. 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. In keeping with this hypothesis is the observation

(21) For early investigations of the mechanism of the Vol'pin reaction, see H. H. Brintzinger, *J. Amer. Chem. Soc.*, **88**, 4305, 4307 (1966).

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

(23) E. E. van Tamelen and D. A. Seeley, *ibid.*, **91**, 5194 (1969).



that the chemical fixation of nitrogen becomes catalytic with respect to titanium (275% NH_3) when aluminum isopropoxide is included in the previously reported reaction of sodium metal with a glyme solution of naphthalene and titanium tetraisopropoxide.

Titanium must be reduced beyond the III state before appreciable amounts of nitrogen are reduced, as shown by a rough calculation of the amount of current having passed through a platinum electrode cell at the point where ammonia could first be detected. Also, in an experiment conducted in a divided cell, the solution in the cathode compartment rapidly turned blue during the electrolysis, suggesting the presence of Ti(III) in the solution. When approximately 1 mole equiv of electrons/mole of titanium had been passed through the cell, the solution started to turn black (indicating titanium(II)), and thereupon ammonia began to appear in bound form. Our observations to date are consistent with the reaction sequences diagrammed in Chart II.

Fixation of N_2 from the Air

That N_2 might, under propitious circumstances, compete with O_2 in a purely chemical reaction with a suitable agent is implied by the well-known fact that such selection seems to occur during the operation of N_2 -fixing legumes, bacteria, and other life forms. This surmise is strengthened by recognition of the known differences in molecular dimensions, nature of the unshared electron pairs, and—perhaps most important—electronic multiplicity of N_2 and O_2 . Encouraged by such considerations, we attempted with our system fixation of N_2 directly from the atmosphere. Although the quantitative aspects of the phenomena are confused by

the high instability of the “active” N_2 -fixing species, the side reaction of O_2 with naphthalide, and the operation of a two-phase (gas-liquid) reaction, our results nevertheless demonstrated clearly, and for the first time, the nonbiological conversion of N_2 as a component of air to NH_3 .

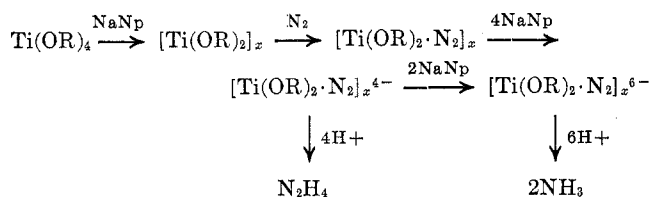
In fixation experiments with air, the general method using titanium(II) isopropoxide was employed, and the active fixation agent was prepared either under argon before exposure to air or under air from the beginning. In the former case yields of fixed ammonia were lower, probably because of the temporal instability of the monomeric Ti(II) species: $\sim 2\%$ of ammonia was formed with air, as contrasted with $\sim 6\%$ with pure nitrogen, both experiments being carried out under otherwise virtually identical conditions with 4.0 equiv of sodium naphthalide. In this preparation, no naphthalide was present, as indicated by esr measurement. When both preparation of lower valent Ti and reaction with N_2 were executed under air, ammonia yields of 10% (3 equiv of naphthalide) and 22% (10–12 equiv of naphthalide) were realized. Thus, it seems clear that the titaniferous N_2 fixer is truly undergoing reaction with N_2 competitively with O_2 .²⁴

Conversion of N_2 to N_2H_4

In the remainder of this Account, we describe our efforts to convert N_2 to products other than NH_3 . In this activity, success was first encountered by virtue of arrested reduction of fixed N_2 on its energetically down-

(24) A. D. Allen and F. Bottomley, *Can. J. Chem.*, **46**, 469 (1968), simultaneously reported the utilization of aerial N_2 in the formation of the $[\text{Ru}^{\text{II}}(\text{NH}_3)_2\text{N}_2]^{2+}$ ion.

Chart III



ward path to NH_3 , made possible no doubt by felicitous formation of a stable transition metal species with a partially reduced N_2 ligand.

Molecular nitrogen, on successive treatment with the transition metal alkoxide-radical-anion system and proton source, generates hydrazine, apparently the first case of substantial transition metal catalyzed conversion of elemental nitrogen to any compound other than ammonia.²⁵ After addition during 15–90 min of tita-



nium(IV) isopropoxide to a stirred THF solution of sodium naphthalide under nitrogen, immediately followed by hydrolysis,¹ there were liberated hydrazine and ammonia in proportions which were dependent upon the ratio of the fixing to the reducing agents. The yield of hydrazine rose with decreasing Ti(IV):NaNp molar ratios to a maximum of 15–19% (based on Ti) at a Ti(IV):NaNp ratio of 1:5–6, while the $2\text{NH}_3:\text{N}_2\text{H}_4$ ratio varied within the range 3.3–5.0.

When any one of the transition metal compounds CoCl_2 , MoCl_5 , WCl_6 , CrCl_3 , NiBr_2 , or FeCl_3 was substituted for titanium(IV) isopropoxide in the experimental procedure described, no hydrazine could be detected as product. Also, no hydrazine apparently was formed when a benzene solution of the $(\text{C}_6\text{H}_5)_2\text{Ti} \cdot \text{N}_2$ dimer was exposed to water, alcohol, aqueous acid, aqueous base, or 2–4 molar equiv of NaNp in THF. Similarly, the $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2$ ion did not generate hydrazine on treatment with limited amounts of NaNp.

Various observations permit a tentative interpretation of the hydrazine-ammonia synthesis sequence. The titanium hydrazine progenitor is subject to further *in situ* reduction, as shown by the increase (to 22) in the $2\text{NH}_3:\text{N}_2\text{H}_4$ ratio after a reaction mixture of the type described above is treated overnight with a large excess of sodium naphthalide. Lack of appreciable molecular nitrogen liberation during the protonation step is consistent with the absence of diimide-level bound nitrogen, which normally would, on protonation, release free diimide, known to disproportionate rapidly to elemental nitrogen and hydrazine. If the foregoing is taken in conjunction with previously acquired knowledge of this system, the relationships expressed in Chart III emerge.

N_2 in the Synthesis of Organic Amines and Nitriles

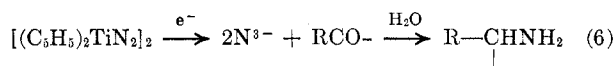
More recently we have developed a reaction system, utilizing dicyclopentadienylnitrogenium dichloride and magnesium metal as starting materials, which permits in one laboratory operation the incorporation of nitrogen from N_2 into various organic carbonyl compounds

by means of an overall reductive deoxygenation process (unpublished results, Dr. H. Rudler). In operation, a solution of Cp_2TiCl_2 in THF is added portionwise to magnesium powder, all under dry N_2 . After 1 hr at 23° , N_2 absorption is complete. An excess of ketone or aldehyde is added to the black solution, and the resulting mixture stirred at room temperature for 5 days.

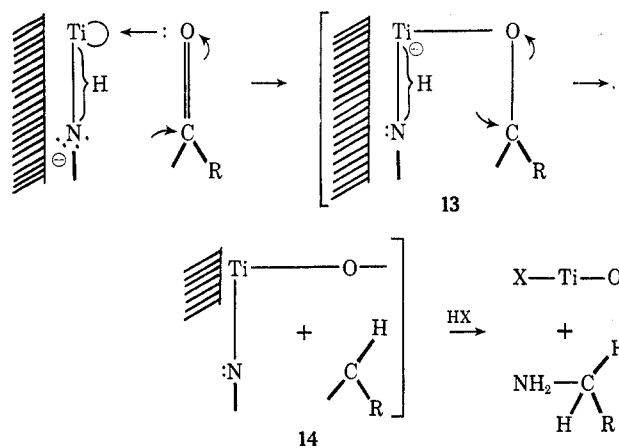


After work-up, a ca. 50% yield of primary and secondary amines is observed. Under these conditions, benzoyl chloride undergoes deoxygenation with incorporation of nitrogen, forming benzonitrile.

In view of the earlier studies on the course of titanium-based nitrogen-fixation reactions and the chronology of the presently described nitrogen incorporation, it seems likely that sequence 6 is operative. Although the exact structural nature of the nitride intermediate



is obscure, a titanium-nitrogen(III) bond may be presumed available at this stage. In that case there exists opportunity for an initial interaction with a carbonyl group in which an unshared electron pair on oxygen is accommodated by empty titanium orbitals while anionic nitrogen attacks carbon. In somewhat the same way as the Wittig reaction progresses, a titaniferous intermediate of type **13** may form and then ring-open with retention of titanium-oxygen and carbon-nitrogen bonds (**14**). Since titanocene hydrogen seems to be available at the termination of a nitrogen-fixation-reduction reaction, it is possible that such hydrogen may be transferred (possibly *via* nitrogen) to α carbon in the amine, as shown. The role of titanium in this overall process may be crucial, as intimated by the above, since other metal nitrides apparently do not undergo C-amination reactions.



I wish to acknowledge with considerable pleasure and satisfaction the collaboration with pre- and postdoctoral organic chemists who have the ability and confidence necessary for progress in a research area of this type. I also express my appreciation to Professor H. Taube for engaging in, since 1962, meaningful and understanding discussion, both prospective and retrospective. Financial support for our research was provided by the National Institutes of Health.

(25) E. E. van Tamelen, R. B. Fechter, and S. W. Schneller, *J. Amer. Chem. Soc.*, **91**, 7196 (1969).