effect, we are now undertaking the preparation and measurement of the ultraviolet ORD of 16 possible dinucleotides to compile base–base interaction parameters at any wavelength. Furthermore, for a better understanding of the molecular geometry of RNA of known nucleotide sequence through extention of the nearest neighbor calculations,[18] it seems essential to obtain some basic information on the conformations of minor base-containing oligonucleotides, since, for example, alanine-specific *t*-RNA and serine-specific *t*-RNA contain 13 and 15% minor nucleotides per molecule,[19,20] and pseudouridine exhibits a small negative Cotton effect while uridine shows a positive Cotton effect.[21]

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[18] See C. R. Cantor, S. R. Jaskunas, and I. Tinoco, Jr., *J. Mol. Biol.*, **20**, 39 (1966).

[19] R. W. Holley, J. Apgar, G. A. Everett, J. T. Madison, M. Marquisee, S. H. Merrill, J. R. Penswick, and A. Zamir, *Science*, **147**, 1462 (1965).

[20] H. G. Zachau, D. Dutting, and H. Feldmann, *Angew. Chem.*, **78**, 392 (1966).

[21] T. L. V. Ulbricht, T. R. Emerson, and R. J. Swan, *Biochem. Biophys. Res. Commun.*, **19**, 643 (1965).

Communications to the Editor

The Formation of $Ru(NH_3)_5N_2^{2+}$ in Aqueous Solution by Direct Action of Molecular Nitrogen

Sir:

Since the discovery[1] of $Ru(NH_3)_5N_2^{2+}$ and the elaboration of the class of N_2 complexes,[2] it has been a goal of our own research on reactions of molecular nitrogen to find a reagent which will combine spontaneously with it in water solutions under mild conditions. The isolation of compounds containing N_2 in combination and formed by the reaction of N_2 with metal complexes in nonaqueous media has been accomplished,[3–5] and these results have encouraged us in our pursuit of the stated goal.

We here report evidence that N_2 reacts spontaneously with $Ru(NH_3)_5H_2O^{2+}$ [6] in aqueous solution at room temperature to form Allen and Senoff's ion. This ion shows a strong absorption at 221 mμ with ϵ 1.3 ± 0.1 × 10^4. A solution containing $Ru(NH_3)_5H_2O^{2+}$ at *ca.* 10^{-3} *M* was prepared by the reduction of $Ru(NH_3)_5Cl_3$ in 0.1 *M* H_2SO_4 by amalgamated Zn and was then separated from the reducing agent. When N_2 is bubbled through the solution the absorption peak at 221 mμ develops, and in several hours the absorption corresponds to *ca.* 50% conversion to Allen and Senoff's ion. The rise in absorption itself does not, of course, prove that molecular nitrogen has been brought into reaction. Proof that reaction with N_2 has indeed taken place was provided by the two lines of evidence which are herewith outlined.

A solution 0.10 *M* in $Ru(NH_3)_5Cl_3$ and 0.1 *M* in H_2SO_4 was treated with amalgamated Zn, and argon was passed through. After 45 min the solution was separated from the residual metal, taking care to exclude air; at this stage it showed no significant absorption in the region of interest. A stream of N_2 was now passed through; absorption in the ultraviolet region began to develop promptly, the peak at 221 mμ first appearing as a shoulder on much stronger absorption at 260 mμ. After 6 hr at room temperature, further increase in peak heights was slow. The stream of N_2 was now replaced by a stream of He, and after 45 min an excess of Ce(IV) was added. Nitrogen, identified by gas chromatography, was liberated. The amount was measured and it was found that between 0.5 and 0.6 molecule of N_2 had been trapped for each mole of Ru(II) which was used. Earlier experiments have shown that Ce(IV) in excess releases N_2 rather cleanly from Allen and Senoff's ion.

In another experiment, amalgamated zinc was added to a solution 0.067 *M* in $Ru(NH_3)_5Cl_3$ and 0.1 *M* in H_2SO_4, and N_2 was passed through for 10 hr. Aqueous ammonia was added to bring the pH to *ca.* 9, and the solution was filtered. After several hours a concentrated solution of sodium tetrafluoroborate was added, whereupon a light yellow solid was obtained. The solid was washed with water, acetone, and ether and dried, and the infrared spectrum was taken. The spectrum closely resembled that of genuine $Ru(NH_3)_5N_2(BF_4)_2$ prepared by the method of Allen and Senoff, and in particular a strong, sharp peak at 2130 ± 10 cm^{-1} was observed. The solid material obtained from reaction with molecular N_2 also was found to release N_2 on being oxidized by Ce(IV). The amount of N_2 corresponded to that which would be expected on the basis of the intensity of the absorption at 221 mμ using the molar extinction coefficient measured for Allen and Senoff's ion to calculate the concentration of $Ru(NH_3)_5N_2^{2+}$ in the direct preparation and making allowance for the liberation of N_2 also by the small amount of the species absorbing at 260 mμ which was present in the solid.

The nature of the species showing strong absorption at 260 mμ is not yet clear to us. We have found that

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

[2] J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966).

[3] A. Yamamato, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

[4] A. Sacco and M. Rossi, *ibid.*, 316 (1967).

[5] The absorption of N_2 by a solution of $RuCl_3$ or $RuCl_3OH$ in THF and treated with Zn has been reported: A. B. Shilov, A. K. Shilova, and Yu. G. Borod'ko, *Kinetika i Kataliz*, 7 (4), 768 (1966); *Chem. Abstr.*, **65**, 19655*b* (1966).

[6] The aquo ion may be partly converted to the sulfato complex in the presence of sulfate ion. The equilibrium between the two forms is labile and will not greatly affect the observations.

when a product solution showing absorption both at 221 and 260 mμ is diluted and made slightly alkaline with NH_3, the band at 221 mμ rises and that at 260 mμ decreases. The interconversion takes place also in acidic solution but less rapidly. Solid material separated from a solution containing a large proportion of the 260-mμ species showed only weak infrared absorption at $\sim$2130 cm^{-1}, but it did liberate N_2 on being oxidized by Ce(IV). Work on these reactions is continuing.

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Direct Ammonia Formation under Mild Conditions by Molecular Nitrogen Reducing Systems Based on Organic Titanium Species

Sir:

Within the area of nitrogen fixation research, earlier investigators have reported the generation of ammonia after acidification of μ-ammino-metal species prepared by room temperature chemical reduction of metal salts of complexes in the presence of molecular nitrogen under generally high pressures.[1] Also, stable coordination compounds carrying N_2 ligands have been identified,[2] and an organic species which captures N_2 has been described.[3] In this communication we report a different mode of molecular nitrogen fixation: the direct formation of volatile ammonia, carried out at room temperature and under atmospheric pressure and brought about by the combined action of a low-valent organic titanium species[4] and an electron source.

Experiments were designed to involve titanium(II).[4] In a typical case, titanium tetrachloride (0.5 mole equiv) was added to a suspension of potassium *t*-butoxide[5] (1.0 mole equiv) in diglyme[6] at 0° under an atmosphere of nitrogen. The suspension of dialkoxytitanium dichloride was allowed to warm to room temperature, and potassium metal (1.0 equiv) was added. Reduction of the Ti(IV) species was evident by the change in color from off-white to intense 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. Within 48 hr after addition of potassium, ammonia was detected in the exit traps. Identification and analysis of ammonia was achieved by vpc,[7] by mass spectrometry,[8] and by titration.[9]

Ammonia production continued for at least several weeks. When volatile ammonia ceased to evolve,[10] addition of further amounts of potassium metal produced more volatile ammonia. Moreover, 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. Yields of volatile ammonia on the order of 10–15% (based on titanium) have been realized. Ammonium ion has also usually been detected when reaction mixtures were subjected to hydrolysis with dilute sulfuric acid.

When argon was substituted for nitrogen in the above experiment, no ammonia was produced. Ammonia (or an ionic counterpart, *e.g.*, amide or nitride) has not been detected in any ingredient of the reactions. Alkali metal, alkali metal alcoholate, and titanium tetrachloride are all necessary materials for the production of volatile ammonia; when any one was omitted from the reaction mixture, no ammonia was detected in the exit gases.

Alkoxide anions other than *t*-butoxide have been utilized with success in that experiments in which potassium *t*-butoxide was replaced with the potassium salts of methanol, 1-hexanol, and phenol all produced volatile ammonia. Experiments of the above type, but involving sodium ethoxide coupled with potassium reduction or potassium *t*-butoxide coupled with sodium reduction, have also produced ammonia. Reduction of dicyclopentadienyltitanium dichloride with sodium naphthalide in THF[11] or diglyme under an atmosphere of nitrogen generated volatile ammonia as well.

On the basis of the following observations, we regard ethereal solvent as the most likely source of hydrogen in the processes leading to volatile ammonia. In experiments in which attempts were made to rigorously exclude water, the yields of volatile ammonia did not observably differ from those characteristic of runs in which no such precautions were taken. Also, the yields of ammonia were not notably affected by changing the nature of the organic unit in the titanium alkoxide. On the other hand, when the reaction was performed in xylene, ammonia was less abundant by an order of magnitude than in the experiments involving ethereal solvents.

We are investigating the mechanism and scope of these reactions.

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(1) M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966), and references cited therein. See also H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305 (1966); **88**, 4307 (1966).

(2) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965); J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966). For the direct incorporation of N_2, see: 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, T. Saito, and K. M. Song, *ibid.*, 419 (1967); A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 3071 (1967); D. E. Harrison and H. Taube, *ibid.*, **89**, 5706 (1967).

(3) D. C. Owsley and G. K. Helmkamp, *ibid.*, **89**, 4558 (1967).

(4) E. E. van Tamelen and M. A. Schwartz, *ibid.*, **87**, 3277 (1965).

(5) The metal alkoxide either was prepared *in situ* from alcohol and alkali metal, or (more conveniently) commercially available reagent was used.

(6) Distilled from sodium metal into the reaction vessel.

(7) Column (6 ft × 0.25 in.) of 20% Carbowax 20M on Porapak Q.

(8) Performed on an Associated Electrical Industries MS-9 high-resolution mass spectrometer. We thank Dr. Alan Duffield for this determination.

(9) N. H. Furman, Ed., "Scott's Standard Methods of Chemical Analysis," Vol. 1, 6th ed, D. Van Nostrand Co. Inc., Princeton, N. J., 1962, p 745.

(10) Completion of ammonia evolution was usually accomplished by warming the reaction mixture.

(11) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **88**, 1138 (1966).