Reply: Standards of Demonstration for the Heterogeneous Photoreactions of N_2 with H_2O

By *Julian A. Davies* and *Jimmie G. Edwards**

The claim that ammonia can be synthesized catalytically from nitrogen and water in the presence of simple metal oxide powders by the action of light suggests a process of overwhelming importance to the future of the human race. For that reason, the possibility deserves our utmost attention. For the same reason, it can be very enticing to conduct large numbers of experiments with various potential catalysts that appear to produce tantalizingly small amounts of ammonia, as has been occurring now for fifteen years. If the small amounts are adventitious and not photosynthetic, all the effort has been wasted, and nothing positive has been added to the human condition. The concept of a major discovery that remains continually on the borderline of demonstration is internally inconsistent. It behooves us, then, to settle this issue now by setting guidelines to decide the validity of this putative process. If the claim is valid, we should proceed to fulfill its stupendous promise of a completely renewable, solar-driven source of ammonia. Our communication[1] gave such guidelines and expressed our skepticism about the validity of the claim.

In the correspondence,[3] the authors object to the procedures and conclusions given in our Communication. We are nonplussed by the statements, "Only an 'intelligent' contamination could explain all the results..." and "...irradiated surface area of catalyst..."[2a] and by the unusual coefficients in Equation (a). [2b] We did note that this choice of coefficients makes the reaction have about the same $\Delta G^{\circ}(298\ \mathrm{K})$ as that of their putative reaction (c). Both correspondents take us to task for not fully referencing prior published work or providing complete experimental details. We followed the "Instructions to Authors" where the page limit (inclusive of all literature citations) and the instruction to summarize experimental details in Communications for *Angewandte Chemie* are clearly stated. Full experimental details of our work are available elsewhere,[3] and more work is to be published in the near future. A complete review by us of the literature in this field has been accepted for publication.[4] Our Communication included only our statistically most significant results, exactly as stated therein.

The correspondents dismiss our results with the assertion that they are possessed of special arts in catalyst synthesis not known to us and that our reaction conditions were somehow unsuitable for the putative photoreaction: "it is difficult to assess whether Edwards et al. had catalytically active powders..."[2a] and "Edwards et al. probably never had active photocatalysts at their disposal".[2b] We confirm unequivocally that no powder that we examined ever showed any statistically significant catalytic activity for the putative photoreaction under discussion here. Despite the claims that only very special substances prepared under highly controlled conditions will catalyze the putative reaction, a vast array of different materials, prepared and characterized by diverse techniques, has been examined for potential photocatalysts of this reaction, and success with them has been reported by many workers.[4] Low levels of ammonia have been reported from reactions that employed vastly different putative catalysts, among them desert sands, and that were performed under very different experimental conditions. It is stated[2a] that "It should be recalled that only homogeneous samples having Fe^{3+} ions in the lattice of TiO_2 are photoactive." The origin of this statement is obscure to us, especially in the light of the work on desert sands (cited in[2a]) whose precise structure and homogeneity are unknown. In connection with this topic, we note that a review article by Augugliaro and Palmisano cites without critical comment a report that boiling chips catalyze the putative photosynthesis of ammonia.[5]

Statistically significant results that unequivocally confirm the photocatalytic synthesis of ammonia from nitrogen and water over oxide catalysts are not found in the literature.[4] If the correspondents are indeed possessed of special arts in catalyst synthesis, then it would be straightforward for them to prepare catalysts that can generate ammonia from $^{15}N_2$ at a level where unambiguous demonstration is routine[3] and where a statistically significant number of experiments can easily be performed. We note the operational technique[2b] ("....numerous samples must be prepared and tested individually prior to the actual photoreduction experiments") where it seems each batch of catalyst was tested and only those that produced the desired result were reported. The authors state that we "claim to have conducted numerous experiments with promising photocatalysts under conditions identical to those used by the earlier investigators." We made no such claim in our Communication. Here we ask both correspondents to publish the specific conditions necessary to prepare effective catalyst powders, and the specific parameters and their values that identify the powders as effective, so that their operational selection method can be avoided.

We believe that no more effort should be expended on production of tiny amounts of ammonia from natural nitrogen as described in most of the published work. We have demonstrated a variety of ways by which adventitious ammonia and various other contaminants can give false indications of ammonia synthesis at such levels.[3] In view of the enormous importance of the putative photoreaction, the cost of isotopically enriched nitrogen gas is small; furthermore, the use of isotope-ratio mass spectrometers in correctly designed, statistically significant experiments can settle the issue conclusively.

After we have been proven wrong in our skepticism, and this new, extraordinarily important way of catalyzing ammonia synthesis has been firmly established, scientists will then face the challenge of understanding the process. In particular, it will be a demanding task to learn how a material as simple as iron-doped titania (or even a boiling chip) can contain sites so special that they organize at least one molecule of nitrogen, three molecules of water, six electrons, six holes, and enough photons to generate the electrons and holes in a way that can drive the reaction uphill by more than 600 kJ mol^{-1}. The energy problem might be worse in Pyrex

---

[*] Prof. J. G. Edwards, Prof. J. A. Davies
Department of Chemistry, University of Toledo
Toledo, OH 43606 (USA)

0044-8249/93/0404-0581 $ 10.00+.25/0

vessels, to which both the correspondents refer, since in such cases only the lower energy photons can contribute to the energy balance. The thermodynamic and kinetic issues we raised in our Communication cannot be rationalized away, despite the argument that our "discussion of the thermodynamics of dinitrogen reduction is [also] seriously flawed and misleading".[2b] The analogy of water photolysis $[H_2O \rightarrow H_2 + 1/2\ O_2]$ is used,[2b] a process that is best conducted photoelectrochemically, and that minimally requires only a single reactant molecule and which can be driven uphill by a single photon of UV radiation unless its equation is balanced in the misleading way of their Equation (a). The analogy fails.

Augugliaro and Soria[2a] raise the issue of photooxidation of ammonia, a process readily catalyzed by every powder we synthesized. This mechanistically fascinating but thermodynamically favorable process has been firmly established since the early work of Gopalarao et al.[6] We observed it whenever we irradiated aqueous ammonia in the presence of gaseous nitrogen and a titania-based powder. We have considered the possibility that titania-based catalysts 1) promote nitrogen reduction at one type of site and ammonia oxidation at a second type of site, or 2) promote nitrogen reduction at one wavelength of incident radiation and ammonia oxidation at a second wavelength; each of these processes would fix nitrogen. However, we found no statistically significant evidence of fixed nitrogen, as reported in our Communication.

In conclusion, we advise those who would continue with this line of research to attend to the standards of demonstration we set in our Communication, this letter, and elsewhere.[3, 4]

---

[1] J. G. Edwards, J. A. Davies, D. L Boucher, A. Mennad, *Angew. Chem.* **1992**, *31*, 489; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 480. The "other work" to which we referred in this paper was in connection with an innovative engine for which one of the proposed fuel systems included ammonia. The criticism in reference [5] of [2a] is unjustified.

[2] a) V. Augugliaro, J. Soria, *Angew. Chem.* **1993**, *105*, 579; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, Nr. 4; b) L. Palmisano, M. Schiavello, A. Sclafani, *ibid.* **1993**, *105*, 581 and **1993**, *32*, Nr. 4.

[3] David L. Boucher, *Ph. D. Thesis*, University of Toledo, **1992**, *Diss. Abstr. Int.* **1992**, *53-B*, 2853.

[4] J. A Davies, D. L. Boucher, J. G. Edwards, *Adv. Photochem.* in press.

[5] V. Augugliaro, L. Palmisano in *Photocatalysis and Environment* (*NATO ASI Ser. Ser.* **1988**, **237**, 432).

[6] G. Gopalarao, C. I. Varadanam, *J. Indian Chem. Soc.* **1941**, *18*, 361 and references therein.