Comment on the Communication "Production of Hydrogen from Interaction of an Anion Radical and Water"

Sir:

In a recent communication, Stevenson and his colleagues reported the formation of molecular hydrogen from the interaction of an anion radical with water. The pertinent reaction was written as $2N^-\cdot + 2H_2O \rightarrow 2N + 2OH^- + H_2$, N denoting naphthalene and $N^-\cdot$ its anion radical. Their claims appear to us misleading and erroneous, and to avoid their perpetuation in the literature we wish to make the following statements.

Stevenson et al. observed evolution of hydrogen gas on addition of water to a thoroughly evacuated solid residue left after solvent evaporation from a tetrahydrofuran (THF) solution of sodium naphthalenide, $N^-\cdot Na^+$. Their observation is correct, although not surprising. Reduction of naphthalene dissolved in THF by metallic sodium yields sodium naphthalenide in a high yield because solvation of the resulting $N^-\cdot Na^+$ ion pairs by THF substantially contributes to the driving force of this process. The resulting *stable* salt has the composition $N^-\cdot Na^+(THF)_n$ and the system comes to equilibrium at ambient temperature when the ratio $[N^-\cdot Na^+(THF)_n]/[N]$ is 20–30. In poorer solvents the degree of reduction is much lower,[2] e.g., in diethyl ether (DEE) the equilibrium ratio $[N^-\cdot Na^+(DEE)_m]/[N]$ is exceedingly low, substantially smaller than 10^{-4}. However, the degree of conversion may be increased by adding THF to the DEE solution, e.g., the equilibrium ratio is ~0.1 when THF is present at 0.45 M concentration because the complex $N^-\cdot Na^+(THF)_2$ is formed then.[2] These observations stress the importance of THF in fostering this reduction.

The THF solvated $N^-\cdot Na^+$ salt retains its integrity and stability as long as the THF vapor pressure exceeds the pertinent saturation pressure. Application of vacuum leads to its desolvation, and, since the nonsolvated salt is unstable, it spontaneously decomposes into naphthalene and metallic sodium. The reaction of the latter with water is well known and yields hydrogen and NaOH.

This eventuality was considered by Stevenson. However, he ruled it out claiming that naphthalene could not be sublimed out from a residue provided that the reduction was completed, whereas sublimation of naphthalene was possible when the reduction was partial, i.e., when the investigated sample contained some free naphthalene.

We dispute their claim. A 10^{-2} M solution of $N^-\cdot Na^+$ in THF was prepared by exhaustive reduction of naphthalene on sodium mirror, the completion of the reaction being checked by spectrophotometric analysis. Such a solution was stored in an evacuated flask A linked to an empty flask B. Subsequent chilling of flask B with liquid nitrogen led to spontaneous distillation of the solvent from A to B, and after a few hours only a residue of metallic sodium was left in A. *All* of the previously reduced naphthalene was quantitatively recovered in B (checked again spectrophotometrically after melting the frozen solvent). This experiment was twice repeated, always with the same result.

Finally, the last sentence of Stevenson's communication calls for comment. He states "The possibility of photogeneration of anion radicals to be used for water cleavage and H_2 production *with recovery of neutral substrate* should not be overlooked." (our italics). This is incorrect. Photochemical or, indeed, *any* reaction converting A into $A^-\cdot$ has to proceed according to an equation $A + X \rightarrow A^- + X^+$. The expected water cleavage would result then from a reaction,

$$2A^- + 2X^+ + 2H_2O \rightarrow 2A + 2X^+OH^- \text{ (or XOH)} + H_2$$
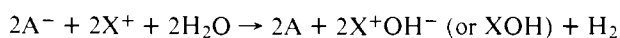
which is equivalent to a process $2X + 2H_2O \rightarrow 2XOH + H_2$,

as exemplified by $2Na + 2H_2O \rightarrow 2NaOH + H_2$ for X = Na. Hence, the cleavage of water and formation of hydrogen has to be associated with conversion of X into XOH and the reagent X needed for water cleavage *is not* regenerated in the process. Thus, the A + X system cannot act as a catalytic and regenerating system in any photolytic cleavage of water with molecular hydrogen formation.

References and Notes

(1) G. R. Stevenson, J. Valentin, C. Meverden, L. Echegoyen, and R. Maldonado, *J. Am. Chem. Soc.*, **100**, 353 (1978).
(2) L. Lee, R. Adams, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **93**, 4149 (1971).

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Catalytic Reductions Using Carbon Monoxide and Water in Place of Hydrogen. 2. Reduction of Aromatic Nitro Compounds to Amines

Sir:

We have recently described several novel catalyst systems capable of effecting the hydroformylation reaction of olefins using carbon monoxide and water in place of hydrogen.[1] We report now the use of related systems which effect the catalytic reduction of aromatic nitro compounds to aromatic amines with carbon monoxide and water (eq 1).

$$RNO_2 + 3CO + H_2O \rightarrow RNH_2 + 3CO_2 \qquad (1)$$
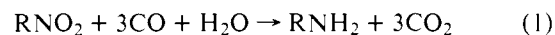
The stoichiometric reduction of aromatic nitro compounds to amines using alkaline solutions of $Fe(CO)_5$ was first reported in 1925,[2] but the exact nature of the reducing agent was not then known. Much more recently, Ladensburg and co-workers[3] have shown that salts of the trinuclear anion, $HFe_3(CO)_{11}^-$, will accomplish the reduction, and Watanabe and co-workers[4] have obtained similar results with salts of the mononuclear anion, $HFe(CO)_4^-$. Each of these hydridoiron carbonyl anionic species can be obtained by the reaction of $Fe(CO)_5$ with an aqueous base and each could then be involved in the reduction first reported.

With $HFe(CO)_4^-$ as the reducing agent, Watanabe and co-workers reported that the reduction remains stoichiometric, rather than catalytic, when conducted under a pressure of carbon monoxide. However, the stoichiometry reported is most remarkable in that 1.8 mol of nitrobenzene is reduced to aniline per mole of $HFe(CO)_4^-$ consumed; since in terms of electron transfer the reduction of nitrobenzene to aniline involves six electrons per molecule, then the $HFe(CO)_4^-$ anion must be acting as an eleven-electron transfer reagent! We have repeated these experiments and have confirmed the results.

Irrespective of the details of the mechanism of the overall reduction,[5] the source of most of these electrons must primarily be the carbon monoxide ligands of the $HFe(CO)_4^-$ anion. This could arise as indicated in eq 2 and 3 in which each carbon monoxide ligand acts as a source of two electrons, and in turn is oxidized to carbon dioxide which is an observed product of the reaction. Upon substantial depletion of the CO ligands, oxidation of the iron atom to Fe^{2+} could provide two further electrons (eq 4, m = 0 or 1). A total of twelve electrons is thus available from $HFe(CO)_4^-$ in this manner.

$$Fe(CO)_5 \xrightarrow[-CO_2]{+OH^-} HFe(CO)_4^- \rightarrow Fe(CO)_4 + H^+ + 2e \quad (2)$$