

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.

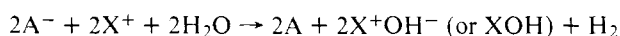
Stevenson et al. observed evolution of hydrogen gas on addition of water to a thoroughly evacuated solid residue left after solvent evaporation from a tetrahydrofuran (THF) solution of sodium naphthalenide, $N^{\cdot-}\cdot Na^+$. Their observation is correct, although not surprising. Reduction of naphthalene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

The THF solvated $N^{\cdot-}\cdot Na^+$ 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 $N^{\cdot-}\cdot Na^+$ 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 $A + X \rightarrow A^{\cdot-} + X^+$. The expected water cleavage would result then from a reaction,



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.

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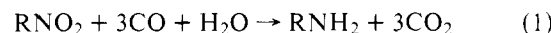
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Catalytic Reductions Using Carbon Monoxide and Water in Place of Hydrogen. 2. Reduction of Aromatic Nitro Compounds to Amines

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).



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-workers³ have shown that salts of the trinuclear anion, $HFe_3(CO)_{11}^-$, will accomplish the reduction, and Watanabe and co-workers⁴ 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.

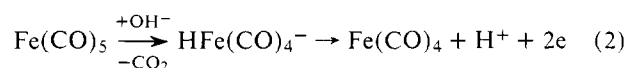
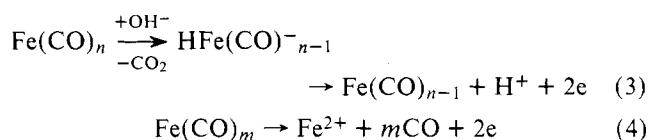


Table I. Catalytic Reactions with Fe(CO)₅^a

Compd (g)	Product	% nitro-arene reduced	% Fe(CO) ₅ remaining ^b
Nitrobenzene (11.0)	Aniline	100	95
<i>m</i> -Dinitrobenzene (8.2)	<i>m</i> -Phenylene-diamine	100	12
2,4-Dinitrotoluene (16.8)	2,4-Diaminotoluene	100	32
2,6-Dinitrotoluene (9.3)	2,6-Diaminotoluene	100	56

^a Reaction conditions: the nitro compound dissolved in 50 mL of glyme was pumped over a 10–12-h period into a stirred 300-mL reaction vessel containing 120 mL of glyme, 6 g of H₂O, 30 g of Et₃N, and 1 g of Fe(CO)₅; the reaction was run at room temperature under 1700 psi of CO. ^b Determined by IR absorption intensities.



Now, since Fe(CO)₄ is readily converted to Fe(CO)₅ with carbon monoxide, but Fe²⁺ is not, it would appear from these equations that the reaction could be made to be catalytic in Fe(CO)₅ if the reaction were to be conducted under a CO pressure in the presence of excess base and under conditions where the irreversible oxidation of Fe⁰ to Fe²⁺ (eq 4) could be prevented.

Following these considerations, we have accomplished the catalytic reduction of several aromatic nitro compounds to the corresponding amines by treatment of the nitro compound with Fe(CO)₅ at 25 °C under 1700 psi of carbon monoxide and in the presence of aqueous glyme containing excess triethylamine. Critical to the success of the catalysis is the need to maintain the concentration of the oxidant low throughout the reaction; presumably this allows the re-formation of Fe(CO)₅ from Fe(CO)₄ in favor of excessive stripping of CO ligands and irreversible loss of catalyst through oxidation to Fe²⁺ as in eq 4. In our experiments this was accomplished by pumping the nitrobenzene slowly into the reactor containing the other reagents over a period of 10–12 h. Even under these conditions a part of the catalyst is usually destroyed giving oxides of iron. The pertinent data are given in Table I.

The data in Table I clearly show that Fe(CO)₅ can be used in a catalytic manner for these reductions; however, the catalyst system is very fragile, owing to oxidative degradation, and would appear to be of little practical value.

The reduction of nitrobenzene to aniline occurs readily with alkaline solutions of Et₄NHFe(CO)₄ maintained at a pH of 12.0; hence, we consider that it is the HFe(CO)₄⁻ anion, rather than H₂Fe(CO)₄, which is the primary reducing agent. We have previously described other polynuclear metal carbonyls which are readily attacked by weak base to generate metal hydride anions and which act as catalysts for the reductive addition of CO to olefins.¹ These systems have also been tested as catalysts for the reduction of nitrobenzene to aniline using CO + H₂O as the reducing agent. As is to be seen from the data given in Table II, several of these species, notably the rhodium, iridium, and osmium clusters, are very effective catalysts for the reduction. The new systems are also far less susceptible to oxidative degradation than is the case for Fe(CO)₅. In each experiment listed in Table II, the nitrobenzene and the catalyst, in a 1000:1 molar ratio, were added to the reaction vessel at the outset and in no case was there any obvious appearance of metal oxides or carbonates at the end. Iqbal has previously reported the catalytic reduction of nitrobenzene to aniline with CO + H₂O using several rhodium

Table II. Reduction of Nitrobenzene with CO + H₂O^a

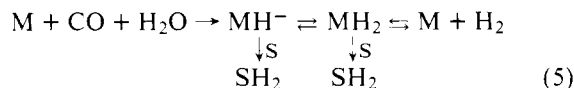
Catalyst	Temp, °C	Time, h	% redn	% H ₂ ^b
Rh ₆ (CO) ₁₆	125	1	100	2–6
Ru ₃ (CO) ₁₂	100	2	71	52
H ₄ Ru ₄ (CO) ₁₂	100	2	73	56
Os ₃ (CO) ₁₂	180	1	100	<3
H ₂ Os ₃ (CO) ₁₀	180	1	100	<3
H ₄ Os ₄ (CO) ₁₂	180	1	100	<3
Ir ₄ (CO) ₁₂	125	1	100	2–6
(Bu ₄ N) ₂ [Pt ₃ (CO) ₆] ₅	125	10	18	<1
Mn ₂ (CO) ₁₀	180	2	20	<2
Re ₂ (CO) ₁₀	180	2	10	<2

^a Reaction conditions: 50.0 mmol of nitrobenzene, 0.05 mmol of catalyst, 35 g of 25% aqueous trimethylamine, and 65 mL of tetrahydrofuran were added to a 300-mL pressure reactor; carbon monoxide (500 psi) was introduced and the reactor heated to a temperature indicated in the table. ^b The percent of hydrogen in the gas phase at the end of the reaction.

derivations, including Rh₆(CO)₁₆.⁶ The plausible suggestion has been made that these, and other reductions with CO + H₂O, proceeds via intermediate generation of hydrogen via the water gas shift reaction (CO + H₂O → CO₂ + H₂) followed by reduction in the usual manner as with hydrogen.⁷ To test this general hypothesis, we have reduced nitrobenzene (11.0 g, 89.4 mmol) in glyme (120 ml) containing D₂O (4.8 g, 240 mmol) under a pressure of hydrogen (830 psi, 350 mmol) and CO (850 psi, 365 mmol), using Fe(CO)₅ as a catalyst. Analysis of the aniline formed (5.2 g) showed a minimum of 88% incorporation of deuterium, thus indicating that at least 80% of the reduction occurred with the CO + D₂O rather than H₂ acting as the reducing agent.⁸

Furthermore, although each of the catalyst systems listed in Table II does produce hydrogen (see last column), nonetheless, the rate of hydrogen production from CO + H₂O generally is very much slower¹ than the rate of reduction of nitrobenzene under similar conditions. For example, the reduction of nitrobenzene with CO + H₂O is two orders of magnitude faster using Os₃(CO)₁₂ than is the water gas shift reaction with this catalyst.

Since metal hydrides are presumably involved as intermediates in the formation of molecular hydrogen from CO + H₂O, and if the same metal hydrides are also the active species in the reduction of any substrate S, then whether a reduction with CO + H₂O proceeds via intermediate hydrogen formation or not will depend on the relative rates of the individual reactions indicated in eq 5. The catalysts listed in Table II are being examined further with respect to this point, but, with the data available so far, it appears that molecular hydrogen does not play an important role.



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- (8) We have shown that, under the conditions of the reaction, there is rapid

exchange of protons and deuterons between aniline and D₂O. Therefore, no more than 20% of the observed reduction could have occurred via H₂. If all of the reduction has occurred via H₂, there would have been observed 59% deuterium incorporation. We have also observed that there is no appreciable exchange between H₂ and D₂O under similar reaction conditions in the absence of nitrobenzene.

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Stabilizing Effect of Dangling Bases on a Short RNA Double Helix as Determined by Proton Nuclear Magnetic Resonance Spectroscopy

Sir:

The secondary structures of naturally occurring RNA molecules contain short helices which are separated by hairpin or bulge loop regions of noncomplementary bases. Attempts to predict the secondary structure of an RNA from its primary sequence have been based on maximizing the amount of double strandedness in the structure.¹ However, for longer RNA sequences, it is difficult to determine which of a number of secondary structures is most stable, since the effect of looped regions on helix stability is not well quantified.

To further probe the factors which affect helix stability, we have undertaken a series of ¹H NMR investigations of several synthetic oligoribonucleotides. The work reported here shows the effect of a terminal "dangling" base on the stability of a short helix. This study offers two advantages over earlier work in this area.^{2,3} Firstly, chemical synthesis of the oligoribonucleotides by the phosphotriester method^{4,5} offers more versatility than enzymatic synthesis, both in the number of sequences available for study, and in scale of preparation. Secondly, the chemical shift and coupling constant data give information about the conformational environment of each constituent nucleotide unit of the molecule. The optical methods used in the earlier studies^{2,3} are limited in this respect, since they can only follow the overall conformational changes of the oligoribonucleotide.

The self-complementary sequence CAUG⁶ was chosen as the reference compound. The procedure of incremental analysis⁷ was used to make the chemical shift assignments. The low field proton resonances of CAUG were assigned by comparison with the 90-MHz spectra of CA, CAU, and AUG, all of which were recorded at 70 °C.⁸ The chemical shift assignments of CAUGA and CAUGU were made in a similar fashion (Table I).

The effect of temperature variation (over the range of 10–70 °C) on the proton resonances of CAUG, CAUGA, and CAUGU was examined. Figure 1 shows a plot of these data for CAUGU. A general nonlinear variation of chemical shifts with temperature was observed in each case and, at the concentrations used in this work,⁹ is associated with the formation of the base paired duplexes. The average melting temperature, *T*_m, of each duplex was determined from those temperature vs. chemical shift curves which showed upfield, sigmoidal shift changes as temperature decreased. The *T*_m values were

CAUG/GUAC, 24 ± 1°; CAUGU/UGUAC, 29.5 ± 1°; CAUGA/AGUAC, 35 ± 1° C

These results clearly indicate that a dangling base stabilizes a double helix, the effect being greater with the dangling A. Preliminary results from work on the duplex formed by the complementary pentaribonucleotides CAAUG and CAUUG (*T*_m, 30 ± 2 °C) indicate that the increase in *T*_m resulting from

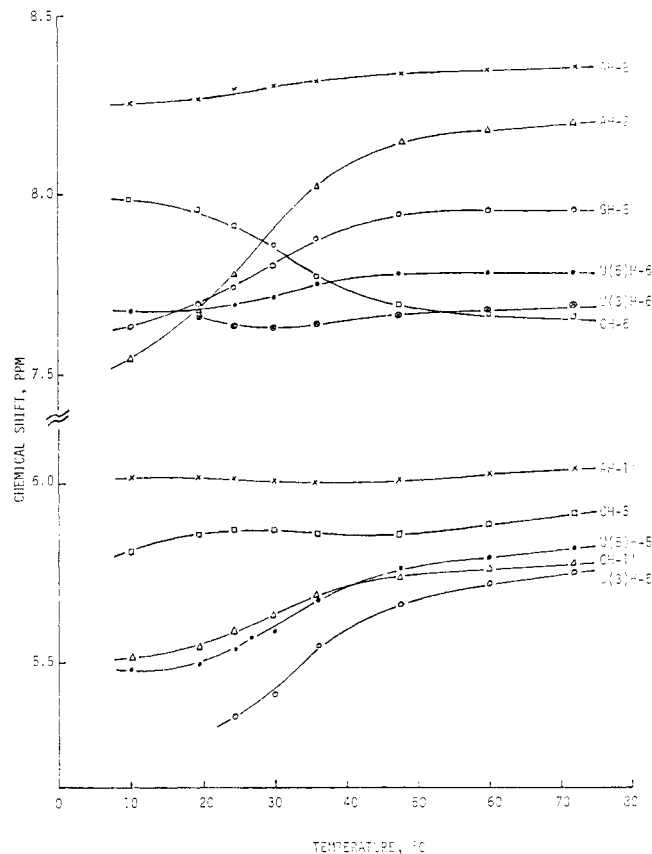


Figure 1. Chemical shift vs. temperature plots for CAUGU.

Table I. Chemical Shifts^a of the Oligoribonucleotides in D₂O^b at 70 °C

Proton	CAUG	CAUGU	CAUGA
CH-6	7.662	7.662	7.649
A(2) H-8	8.346	8.352	8.339
A(2) H-2	8.196	8.199	8.167
U(3) H-6	7.692	7.692	7.699
GH-8	7.962	7.958	7.890
U(5) H-6		7.783	
A(5) H-8			8.316
A(5) H-2			8.180
CH-1'	5.765	5.772	5.721
A(2) H-1'	6.039	6.037	6.053
U(3) H-1'	5.845	5.849	5.779
GH-1'	5.813	5.796	5.764
U(5) H-1'		5.853	
A(5) H-1'			6.053
CH-5	5.912	5.912	5.897
U(3) H-5	5.738	5.749	5.741
U(5) H-5		5.813	

^a Chemical shifts are in parts per million downfield from DSS using *tert*-butyl alcohol-*OD* as an internal reference and are accurate to ±0.005 ppm. ^b pD 7.0 concentrations: CAUG, 9.2 × 10⁻³ M; CAUGA, 9.2 × 10⁻³ M; CAUGU, 7.7 × 10⁻³ M.

an additional internal A·U base pair is similar to the increase that would result from having a dangling U at each terminus, and *less than* the result from having a dangling A.

For duplexing to occur with short oligoribonucleotides each single strand is probably close to a fully stacked conformation,^{12,13} while for long-chain oligoribonucleotides the strands probably have a high percentage of stacked conformers prior to and concomitant with duplexing. Uhlenbeck previously proposed that the dangling base increased favorable stacking interactions between the bases involved in base pairing.² We now have evidence of the base-stacking interaction between duplex and dangling base.