Reduction of Water to Hydrogen by Reduced Polypyridine Complexes of Ruthenium

Sir:

Estimated redox potentials for the charge-transfer excited-state $Ru(bpy)_3^{2+*}$ (bpy is 2,2′-bipyridine)

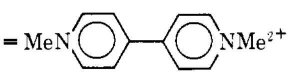
$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{3+} + e: \quad E = -0.84\ V\ (vs.\ NHE) \quad (1)$$

$$Ru(bpy)_3^{2+*} + e \rightarrow Ru(bpy)_3^{+}: \quad E = +0.84\ V\ (vs.\ NHE) \quad (2)$$

show that it is thermodynamically capable of both oxidizing water to oxygen and of reducing water to hydrogen at pH 7.[1-6] Neither reaction occurs by simple photolysis, but the redox properties of the system can be enhanced by ~0.4 V by oxidative quenching to give $Ru(bpy)_3^{3+}$, e.g.,

$$Ru(bpy)_3^{2+*} + PQ^{2+} \longrightarrow Ru(bpy)_3^{3+} + PQ^{+} \quad (3)$$

PQ^{2+} =



or by reductive quenching to give $Ru(bpy)_3^{+}$, e.g.,

$$Ru(bpy)_3^{2+*} + Me_2NC_6H_4Y \rightarrow Ru(bpy)_3^{+} + Me_2NC_6H_4Y^{+} \quad (4)^{2,8}$$

The two enhancements can be obtained simultaneously if the excited state undergoes a disproportionation,

$$2Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{+} + Ru(bpy)_3^{3+} \quad (5)$$

a reaction which can be catalyzed chemically.[9] Electrochemical studies[10] in acetonitrile show that $Ru(bpy)_3^{2+}$ undergoes three reversible one-electron reductions giving successively $Ru(bpy)_3^{+}$ ($E_{1/2} = -1.33$ V), $Ru(bpy)_3^{0}$ ($E_{1/2} = -1.52$), and $Ru(bpy)_3^{-}$ ($E_{1/2} = -1.77$ V) showing that multiply reduced states are also accessible to the system.

Given that $Ru(bpy)_3^{2+*}$ can be reductively quenched and the strongly reduced complex results, it should be possible to devise photocatalytic cycles for reducing water to H_2 either by a direct reaction with water or by driving a secondary redox couple[12] for the H_2 evolution step. We have carried out a series of experiments where reduced polypyridyl complexes of ruthenium are generated by electrochemical reduction in acetonitrile followed by the addition of aqueous solutions at various pH values, and the results are described here.

Solutions of $Ru(bpy)_3^{+}$, although air sensitive, can be generated quantitatively under argon by controlled potential electrolysis at −1.42 V as shown by coulometry followed by reoxidation to $Ru(bpy)_3^{2+}$. Reduced solutions are stable in the absence of air for a period of at least several hours. $Ru(bpy)_3^{0}$ can also be generated electrolytically (at −1.65 V) but is less soluble and precipitates from acetonitrile solutions which are appreciably more concentrated than 0.1-0.2 mM as a dark solid.

Addition of deaerated aqueous solutions at various pH values to $Ru(bpy)_3^{+}$ in acetonitrile causes a color change which occurs on the time of mixing in acid solution (pH 1) but becomes successively slower as the pH is raised. The spectral and electrochemical properties of the resulting solutions are consistent with the quantitative production of $Ru(bpy)_3^{2+}$. However, there is no or very little production of H_2, and we assume that acetonitrile is reduced under these conditions.[13]

In dramatic contrast to the results obtained with $Ru(bpy)_3^{+}$, and apparently illustrating the mechanistic value of a multiple electron-transfer site, the addition of aqueous solutions to $Ru(bpy)_3^{0}$, either in the solid state or in solution, results in the stoichiometric production of hydrogen. When deaerated (Ar bubbling), aqueous solutions having various pH values are added to acetonitrile solutions (~95% CH_3CN-5% H_2O v/v after mixing) containing electrogenerated $Ru(bpy)_3^{0}$, H_2 is evolved. The evolved gas was shown to be H_2 using low temperature (ethanol-dry ice) gas chromatography by sampling the atmosphere above the stirred solutions after water had been added. The amount of H_2 evolved was determined quantitatively by measuring volume changes following the addition of water. The results obtained expressed as the ratio of H_2 produced to moles of electrogenerated $Ru(bpy)_3^{0}$ (as determined by coulometry) follow: pH 1 (added $HClO_4$), 0.96; pH 7 (H_2O), 1.04; pH 12 (added $[N(n\text{-}C_4H_9)_4]OH$), 1.00. Similar results were obtained by adding aqueous acetonitrile solutions to $Ru(bpy)_3^{0}$ either as a solid or dissolved in deaerated butyronitrile. Optical spectra after H_2 evolution was complete suggested that $Ru(bpy)_3^{2+}$ was regenerated quantitatively, but it should be noted that the spectral experiment may not be sufficiently sensitive to detect partial hydrogenation of one of the 2,2′-bipyridyl ligands.[14]

That the source of evolved hydrogen is solvent and not complex was shown by adding D_2O rather than H_2O as the source of water. Mass spectrometric analysis showed that the isotopic composition of the evolved gas was the same within experimental error as that obtained in a blank experiment where D_2 was generated electrolytically from the same sample of D_2O.

The experiments described above show that the stoichiometries of the net reactions between $Ru(bpy)_3^{0}$ and water are

$$Ru(bpy)_3^{0} + 2H^{+} \rightarrow Ru(bpy)_3^{2+} + H_2 \quad (6)$$

$$Ru(bpy)_3^{0} + 2H_2O \rightarrow Ru(bpy)_3^{2+} + H_2 + 2OH^{-} \quad (7)$$

in acidic and basic solutions, respectively. Experiments with closely related polypyridyl complexes like $Ru(trpy)_2^{2+}$ (trpy is 2,2′,2″-terpyridine, Ru $(phen)_3^{2+}$ (phen is 1,10-phenanthroline), and $Ru(bpy)_2(py)_2^{2+}$ show that the chemistry which occurs following the addition of water to solutions containing the electrochemically reduced complexes can be complicated. Initial experiments have given evidence for pathways involving ligand reduction, solvent reduction, and loss of ligands, all of which can be in competition with the production of H_2.

At this point we have no detailed mechanistic information about the reactions which give hydrogen, but we have made certain qualitative observations which are of value. Following the addition of the aqueous solution to solutions containing $Ru(bpy)_3^{0}$, a change in color occurs from that characteristic of $Ru(bpy)_3^{0}$ which is paralleled by hydrogen evolution. The initial color change is complete in the time of mixing at pH 1, within a few seconds at pH 4, and only after several minutes at pH 12. Given the redox potentials of the couples involved and the qualitative estimate of rates, the reactions may be too rapid to occur via the production of free H·.[15] The observation that D_2 is the only product when the solvent consists of 85% CH_3CN-15% D_2O also supports this conclusion since, if the reaction had proceeded via free D·, HD should have appeared as a major product by H-atom abstraction from acetonitrile.[16] However, the most striking point is the obvious value in having a two- rather than a one-electron reduction site. In this context it is interesting to note that, although both $Ru(bpy)_3^{+}$ and $Ru(bpy)_3^{0}$ are capable of acting as two-electron reductants,

$$Ru(bpy)_3^{+} \rightarrow Ru(bpy)_3^{3+} + 2e: \quad E = 0.0\ V\ vs.\ NHE$$

$$Ru(bpy)_3^{0} \rightarrow Ru(bpy)_3^{2+} + 2e: \quad E = 1.42\ V\ vs.\ NHE$$

$Ru(bpy)_3^{0}$ is a far stronger two-electron reductant thermodynamically.

It could be argued that the requirement of a two-electron reducing capability rules out a direct H_2O-splitting scheme

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based on one-electron transfer quenching, but such conclusions should be reached with care. For example, in a dimeric system like $(trpy)(bpy)Ru(L)Ru(bpy)(trpy)^{4+}$ (L = 4,4′-bipyridine) the intermolecular ligands are weakly coupled electronically. Following one-electron reduction, the equilibrium,

$$2[LRu\text{-}RuL]^{3+} \rightleftharpoons [LRu\text{-}RuL]^{2+} + [LRu\text{-}RuL]^{4+}$$

for which $K \sim 1/4$,[17] would be quickly established giving rapid access to a two-electron reduced product.

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Design of Reaction Systems Exhibiting Overshoot–Undershoot Kinetics

Sir:

As a result of intensive research in the last decade, a number of systems showing oscillatory behavior have been found.[1] However, there is no clear-cut experimental example of a chemical reaction in which the concentration of an intermediate shows a few extrema in time as equilibrium is approached.[2] This kinetic phenomenon has been termed by Higgins[3] as "overshoot-undershoot" kinetics. We conjectured that such a phenomenon would occur upon addition of an appropriate reagent to a clock reaction system.

In such a system a halogenate ion oxidizes a substrate. If the halogenate is in excess, free halogen is formed suddenly after a long time lag. The appearance of free halogen corresponds to consumption of the substrate. The concentration of halogen changes according to a saturation curve, while the concentration of halide ion shows a maximum. We surmised that, upon perturbation of this system by a reactant which enters into a substitution reaction with the halogen, the concentration of the halide ion might exhibit two maxima and that of the halogen one maximum. We found that malonic acid is a suitable perturbing reactant.

In our experiments the reaction was followed by spectrophotometric determination of halogen and by monitoring the halide ion concentration using halide-selective electrodes.[4] As it appears from Figure 1, the addition of malonic acid to different clock systems resulted in the appearance of three extrema in the halide ion concentration vs. time curves.[5] The bromate-ascorbic acid-malonic acid system was studied in detail. The original clock reaction can be quantitatively described by the following three equations:[6]

$$BrO_3^- + 3H_2A \rightarrow Br^- + 3A + 3H_2O \qquad (1)$$

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (2)$$

$$H_2A + Br_2 \rightarrow A + 2Br^- + 2H^+ \qquad (3)$$

(where H_2A stands for ascorbic acid and A for dehydroascorbic acid). For these reactions the following rate equations have been determined:

$$v_1 = -d[BrO_3^-]/dt = k_1[BrO_3^-][H_2A] \qquad (1')$$

$$v_2 = -d[BrO_3^-]/dt = k_2[BrO_3^-][Br^-][H^+]^2 \qquad (2')$$

$$v_3 = -d[Br_2]/dt = k_3[Br_2][H_2A] \qquad (3')$$

Reaction 1 can not be studied separately and, assuming the second-order rate equation (1′), Bognar[6] could give only a maximum value for k_1 ($k_1 < 3.3 \times 10^{-3}$ M^{-1} s^{-1}). Reaction 2 has been thoroughly studied,[7] and the values for k_2 given by the different authors are in good agreement considering the different experimental conditions. According to our experiments the value of k_2 at 25 °C and at $I = 1.0$ ionic strength is 3.6 M^{-3} s^{-1}.[8] The bromine oxidation of ascorbic acid is a very fast reaction. No rate data are available in the literature. According to our stopped-flow experiments, when the concentration of both bromine and ascorbic acid is 0.06 M, the reaction is complete within 10 ms. It follows that $k_3 \gg 2 \times 10^3$ M^{-1} s^{-1}. In the presence of malonic acid, only its bromination reaction should be considered. This has been extensively studied. There is general agreement that the rate-determining step is slow enolization of malonic acid which is followed by the fast addition of bromine to the enol:

$$(H_2M)_{keto} \rightleftharpoons (H_2M)_{enol} \qquad (4)$$

$$(H_2M)_{enol} + Br_2 \rightarrow HBrM + Br^- + H^+ \qquad (5)$$

Accordingly the rate of the bromination of malonic acid is given by the following equation:

$$v_4 = -\frac{d[Br_2]}{dt} = \frac{k_4k_5[Br_2][H_2M]}{k_{-4} + k_5[Br_2]} \qquad (4')$$

At higher bromine concentrations the rate is independent of bromine concentration, and the pseudo-first-order rate constant is equal to k_4. According to Leopold and Haim[9] the value

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