Chemical Reduction of Viologen Bisphosphonate Dibromide by Aluminum Foil, Magnesium Turnings, and Mossy Zinc in Dilute Aqueous Hydrofluoric Acid Solution

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The viologen bisphosphonate dibromide {$(HO)_2P(O)$-CH_2CH_2(bipyridinium)$CH_2CH_2(O)P(OH)_2$}Br_2 is a precursor of zirconium viologen bisphosphonate dibromide, $Zr(O_3PCH_2CH_2$(bipyridinium)$CH_2CH_2PO_3)Br_2$, believed to be the active unit in the reversible photochromism of the layered zirconium compound.[1] In general, coloration of alkylviologen dihalide compounds is attributed to the cation radical derived from the reduction of the alkyl viologen component.[2-4] Interest in this area has intensified due to the potential use of the dialkylviologen compounds in solar energy harvesting devices,[2-8] as redox indicators in photosynthetic study,[9-12] as reductants for hydrogen generation from protons,[1,13] and as electron mediators in sensitized redox reactions.[22] It is important to note, however, that in all alkylviologen halide compounds, the halide ions are required to stabilize the charge of the viologen group.[3] The blue color produced in these redox systems show bands around 405 and 605 nm, typical of viologen radical cations.[18-20] Further, purple aggregates of viologen radical cations that exhibit bands at 380 and 540 nm[3] have been detected in complex systems.[3,21,22]

Chemical reduction of dialkylviologens has also been accomplished.[14-17] A recent report indicates that when zirconium bisphosphonate viologen dibromide is treated with dithionite in a basic medium the peripheral alkyl-viologen units are reduced to blue radical cations.[1] In contrast to photoreduction of alkylviologen dihalides where extensive data exists,[2] the literature on direct metal reduction of these compounds, especially in acidic aqueous media, is scarce. Notwithstanding, various attempts have been made in the past to produce isolable quantities of radicals by chemical means using metal granules or powder.[24] Some remarkable experiments performed in this regard entail the use of alkali metal to reduce a halide,[24] and the use of granular magnesium, powdered aluminum, and zinc dissolved in molten pyridinium iodide to produce pure radical by thermal method.[24,25]

This paper reports the first observation of the reduction of a viologen bisphosphonate dibromide by aluminum foil, magnesium turnings, and mossy zinc in a dilute aqueous hydrofluoric acid solution as a new route to radical cation production without stabilizers, sensitizers, or temperature treatment. Alkylviologen radical cation has been known to play an important role in the photochemical reduction of water to yield hydrogen.[3,29] Chemically reduced viologens may also facilitate the production of hydrogen from water in presence of a suitable catalyst such as colloidal platinum.[3,29]

Synthesis of Viologen Bisphosphonate Dibromide. The preparation of this compound has been described previously.[4] In this study, it was prepared as follows: A 0.902 g (0.006 mol) sample of 4,4'-dipyridyl (Aldrich Chemical Co.) was added to 50 mL of water and stirred for about 4 h. Diethyl (2-bromoethylphosphonate (Aldrich, 2.930 g, 0.010 mol) was dissolved in another 50 mL of water. The dipyridyl mixture was stirred into the phosphonate solution in a three-neck, round-bottom flask fitted with a stirrer, reflux condenser, and thermometer. The temperature of the mixture was raised gradually until it dissolved. The solution was refluxed with stirring for 15 h. A 15 mL solution of hydrobromic acid (48%, from Fisher) was added and refluxed for an additional 2 h. The solution was then transferred to an open beaker and heated almost to dryness. The solid was recrystallized twice from water/2-propanol mixture (1:1) and dried in a vacuum desiccator over calcium sulfate/cobalt chloride for several days (weight 2.47 g). Infrared, ^{1}H NMR, and elemental analysis data: IR (mull), 3378, 2921, 1634, 1556, 1454, 1370, 1277, 1142, 1007, 931, 812, 711, 492 cm^{-1}; ^{1}H NMR in deuterium oxide, 2.2 ppm (multiplet) due to 4,4'-dipyridine protons, 4.3 ppm (multiplet) due to OH protons, 8.3 ppm (doublet) and 9.1 ppm (doublet) due to ethylenic protons; elemental analysis (%) by a commercial analytical company calculated (found) C, 31.48 (30.86); H, 3.77 (3.78); N, 5.25 (5.09); Br, 29.92 (29.89) agrees fairly well with published data for viologen bisphosphonate dibromide.[4,19] All solutions were

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Figure 1. (a) Purple film on aluminum foil. (b) Resultant blue solution.

prepared in water purified with Culligan Series E Reverse Osmosis, UV Water Purifier, System 23.

Reduction Procedure. The reduction experiment was performed by immersing a strip of aluminum (Reynolds 657 standard foil) in a dilute aqueous hydrofluoric acid solution of viologen bisphosphonate dibromide. Some quantities of magnesium turnings and mossy zinc (Fisher) were placed in different beakers containing solutions of equal concentrations. A regular solution contains 0.230 g of the compound in 50 mL of water and 2 drops of hydrofluoric acid (52–55%, from Fisher). In a typical experiment, we found that (1) the metal surfaces were initially covered with a purple film (Figure 1a), magnesium and zinc reacting faster than aluminum, (2) blue species gradually migrated away from the surface into the solution, producing blue solutions in the case of aluminum foil and magnesium (Figure 1b), (3) no blue species were observed in the zinc solution under the conditions of this experiment, (4) the aluminum foil solution retained the blue coloration longer than that of magnesium, (5) nickel, tin, iron, lead, and platinum did not react, (6) no coloration by any metal was observed in nonaqueous media such as acetonitrile, pyridine, dry methanol, and 2-propanol where the compound is slightly soluble, (7) when the aluminum foil was removed from the blue solution, the latter gradually turned colorless due to the oxidation of the radical cation by oxygen in the air, (8) under anaerobic condition the purple species on the foil remained indefinitely, (9) aqueous solutions of the compound containing hydrobromic acid, acetic acid, sulfuric acid, hydrochloric acid, and sodium hydroxide did not show analogous results with these metals, (10) the same results were obtained when the experiments were performed in a plastic beaker, precluding the involvement of any component of glass produced by etching (if any) in the reaction, and (11) aluminum, magnesium, and zinc salts did not react.

It is noteworthy that addition of the acids listed in (9) to dilute aqueous hydrofluoric acid solution of this compound yielded blue colors that were decolorized at different rates. In this study we did not attempt to optimize experimental conditions such as amount of metal, concentration of solution, etc., to obtain a maximum yield of radical cation, our attention being centered on the comparable ease and efficiency of radical cation production. Details of the kinetics and mechanism of this reaction under various conditions will be reported elsewhere.

Detection of Hydrogen Gas. A regular solution of the compound (about 3 mL) containing hydrofluoric acid was placed in a test tube containing a strip of aluminum foil. The test tube was covered with a rubber stopper to allow any gas evolved to accumulate. The setup was placed in the hood. A lighted splint was brought to the mouth of the test tube after the stopper was removed. A sharp "pop" (slight explosion) indicated the presence of hydrogen gas.

Discussion. We can envisage two alternative possibilities for the observations reported here:

(i) That dimeric and monomeric forms of alkylviologen radical cation exist simultaneously on the surface of the metal and in solution,[18] respectively. The etching ability of the fluoride ion is well-known. On the other hand, aluminum can retain an oxide film on its surface better than magnesium or zinc due to the inherent reactivity of the latter two metals. Additionally, aluminum can be etched electrochemically.[26-28] On the basis of the foregoing, a reasonable interpretation of our observation is that an equilibrium process is first established between hydrofluoric acid and water:

$$HF(aq) + H_2O \rightleftharpoons H_3O^+ + F^-_{(aq)} \quad (1)$$

This is followed by the etching of the aluminum foil by the fluoride ion:

$$Al(s) + 4F^-(aq) \rightarrow AlF_4^- + 3e^- \quad (2)$$

AlF_4^- is kinetically well defined in aqueous solution.[30] Two moles of these electrons reduce two moles of protons to one mole of hydrogen gas. The evolution of hydrogen gas was confirmed by the standard test (see Experimental Section). Probably in a very fast reaction step, viologen bisphosphonate dibromide molecules undergo a one-electron reduction to yield monomeric radical cations that form dimeric radical cations (purple) on the surface of the aluminum foil:

$$2(V^{2+}2Br^-) + 2e^- \rightarrow (V^+2Br^-)_2 \quad (3)$$
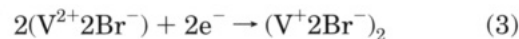
It has been shown that methylviologen cation radicals can complex with a metal (such as mercury) surface.[18] The sum of eqs 2 and 3 gives the net equation for the reaction on the surface of the foil:

$$6(V^{2+}2Br^-) + 2Al(s) + 8F^-(aq) \rightarrow$$
$$3(V^+2Br^-)_2 + 2AlF_4^-(aq) \quad (4)$$
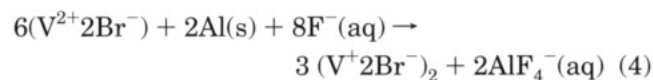
As the foil dissolves, the dimer radical cations are released from the surface and dissociate into monomeric reduced alkylviologen radicals (blue) in solution as shown in eq 5.

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$$3(V^+2Br^-)_2 \rightarrow 6(V^+2Br^-) \tag{5}$$
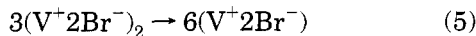
Similar equations can be written for the other reactive metals. Figure 2 shows the UV−visible spectra of the colorless and the blue solutions. The bands at 398 and 599 nm are close to those reported for viologen radical cation in the literature.[3b,16]

(ii) That the reduction process precedes the reaction between the bromide ion and the radical cation, resulting in the formation of an insoluble purple solid on the surface of the metal. This concept was used to explain the principle of an electrochromic display based on a redox reaction of an alkyl viologen dibromide.[21] In accord with our observation, water is essential for this reaction to ensue.

Our focus is directed toward delineating the more feasible view through carefully planned experimentation. Currently, we are studying the reactivity of other halogen compounds of bisphosphonate viologen with the aim of determining the role of halogens in this process and the reactivity of these metals toward other alkyl-viologen derivatives. This observation encourages further work geared toward the utilization of this relatively simple and economical system for the efficient reduction of water in presence of suitable catalysts such as colloidal platinum[29] to produce hydrogen for use in fuel cells, the reduction of organic substrates,[3] etc.
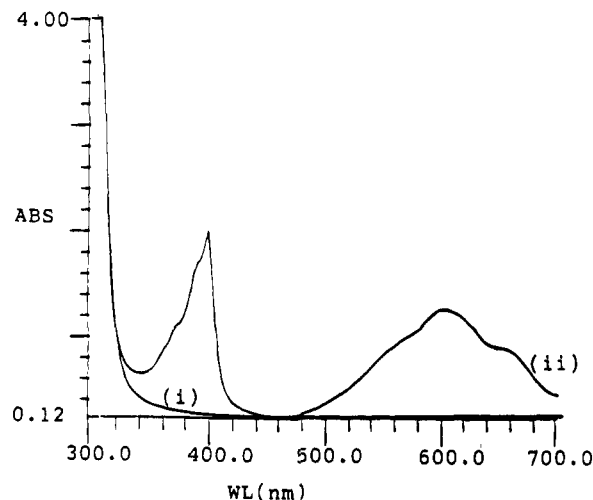

Figure 2. UV−visible spectra of (i) colorless solution before reduction and (ii) blue solution after reduction.