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Reaction of tris(bipyridine)ruthenium(III) with hydroxide and its application in a solar energy storage system

(dioxygen production/water oxidation/dihydrogen formation/hydroxyl radicals/photosynthesis)

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ABSTRACT **Irradiation of $Ru(bipy)_3^{2+}$ (bipy = 2,2′-bipyridine) with light below 560 nm results in the formation of a charge-transfer excited state potentially capable of reducing water to dihydrogen with concomitant production of $Ru(bipy)_3^{3+}$. The latter may be reduced by hydroxide**

$$Ru(bipy)_3^{3+} + OH^- = Ru(bipy)_3^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O$$

to form dioxygen and regenerate the starting complex. The use of these reactions in a cell designed to bring about the photochemical decomposition of water is proposed.

The stoichiometry, kinetics, and mechanism of the $Ru(bipy)_3^{3+}$-hydroxide reaction have been investigated by conventional and stopped-flow spectrophotometry. The dioxygen yield is a sharp function of pH, attaining its maximum value (about 80%) at pH 9. At low pH (3 and 4.8) the production of ruthenium(II) is first order with $k_{obsd} = (1.41 \pm 0.04) \times 10^{-4}$ sec^{-1} (25°, ionic strength $\mu = 1.00$ M with sodium sulfate). In the intermediate pH range (7.9–10.0) complex kinetics are observed. In the hydroxide range 0.01–0.50 M, ruthenium(II) production is predominantly first order with $k_{obsd} = k_a[OH^-] + k_b[OH^-]^2$ sec^{-1}; $k_a = 148$ M^{-1} sec^{-1} and $k_b = 138$ M^{-2} sec^{-1} (25°, $\mu = 1.00$ M, sodium sulfate). For the k_a term, the activation parameters are $\Delta H^\ddagger = 15.3 \pm 1.0$ kcal mol^{-1} and $\Delta S^\ddagger = 7 \pm 3$ cal deg^{-1} mol^{-1} (1 cal = 4.184 J). An intermediate species (λ_{max} 800 nm) forms at the same rate as ruthenium(II) in this hydroxide range. It disappears with $k_{obsd} = 1.2 + 1.1 \times 10^2 [OH^-]$ sec^{-1} at 25°. Similarly absorbing (λ_{max} 750 to 800 nm) species are generated by the addition of hydroxyl radical to $M(bipy)_3^{2+/3+}$ [M = Fe(II), Os(II), Ru(II), Cr(III), Ru(III)] in pulse radiolysis experiments. The kinetics above pH 7 are described in terms of rate-determining nucleophilic attack by hydroxide on the bound bipyridine ring. The hydroxide adduct so generated is tentatively identified with that observed in the pulse radiolysis experiments with $Ru(bipy)_3^{2+}$.

For reduction of $Ru(bipy)_3^{3+}$ by hydrogen peroxide ruthenium(II) production is first order with $k_{obsd} = k_c[HO_2^-] + k_d[H_2O_2]$ where $k_c = 5.4 \times 10^7$ M^{-1} sec^{-1} and $k_d = 8.3$ M^{-1} sec^{-1} (25°, $\mu = 1.00$ M, pH 3.5 to 9.7). This reaction produces dioxygen in 83 ± 15% yield at pH 6.8 and in 1.0 N sulfuric acid.

The photodecomposition of water into its elements is one of the most attractive means of storing solar energy. This decomposition process may be broken down conceptually into three steps: light absorption, water oxidation, and water reduction. Certain transition metal complexes, by virtue of their high absorption in the visible region and their facility in undergoing oxidation-reduction reactions, should be capable of mediating some or all of these processes.

Tris(bipyridine)ruthenium (and related) complexes possess particularly desirable qualities in this regard. Irradiation of $Ru(bipy)_3^{2+}$ (bipy = 2,2′-bipyridine) with light below 560 nm results in the formation of a relatively long-lived [lifetime $\tau = 0.6$ µsec in water at 25° (1)] charge-transfer excited state [$^*Ru(bipy)_3^{2+}$] (2, 3) potentially capable of reducing water to dihydrogen (1), Eq. 1.

$$^*Ru(bipy)_3^{2+} + H_2O = Ru(bipy)_3^{3+} + \tfrac{1}{2}H_2 + OH^- \quad [1]$$

For the complex to function in a catalytic role, the $Ru(bipy)_3^{3+}$ produced when the dihydrogen is generated must be rapidly reconverted to the initial, photoactive species. This may be accomplished through its reduction by hydroxide ion (4, 5) according to Eq. 2.

$$Ru(bipy)_3^{3+} + OH^- = Ru(bipy)_3^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \quad [2]$$

In this way absorption of light in the visible may lead to a net decomposition of water into dihydrogen and dioxygen.

There are additional reasons for interest in reaction 2. The oxidation of hydroxide by relatively mild oxidants is rather unusual (6)[a] and poses mechanistic questions relevant to the production of dioxygen in photosynthetic systems. In this paper, we report a study of the stoichiometry, kinetics, and mechanism of the reaction of $Ru(bipy)_3^{3+}$ with water and hydroxide ion and describe how reactions of this type might be used in solar energy storage systems.

MATERIALS AND METHODS

Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate was purchased from G. F. Smith and recrystallized from water before use. The ruthenium(III) complex $Ru(bipy)_3(ClO_4)_3$ was prepared by oxidation with lead(IV) dioxide, cerium(IV), or chlorine in 0.5 M sulfuric acid and recrystallized once from cold 0.5 M sulfuric acid before use. The ruthenium(III) salt was stored in the dark at 0°. All measurements were made in sodium sulfate media with ionic strength $\mu = 1.00$ M.

The rate of reduction of $Ru(bipy)_3^{3+}$ above pH 11.5 was studied on a Durrum Stopped-Flow spectrophotometer with hydroxide in at least 30-fold excess. The ruthenium(III) solutions were prepared by dissolving the solid immediately prior to use. Formation of ruthenium(II) was monitored at 452 nm and, for high ruthenium(III), at 490 nm. Plots of log $(A_\infty - A_t)$ (the solution absorbance values at times ∞ and t, respectively) versus time were linear to 90% and 80% reaction at those two wavelengths,[b] respectively. Values of k_{obsd},

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Abbreviations: k_{obsd}, pseudo first-order rate constant; bipy, 2,2′-bipyridine; Ru(III) refers to $Ru(bipy)_3^{3+}$; Ru(II), $Ru(bipy)_3^{2+}$.

[a] For $Ru(bipy)_3^{3+/2+}$, E° = 1.26 V. The E° values for iron-, ruthenium-, and osmium-tris(bipyridine) derivatives [which also undergo hydroxide reduction (6)] lie in the range 0.8 to 1.3 V (7).

[b] After the absorbance change is 90% complete at 452 nm (and 80% complete at 490 nm) a very slow, hydroxide-dependent increase in absorbance occurs. This slow process first becomes noticeable at about t_{max} for the 800 nm intermediate (*vide infra*) and is probably related to its decomposition.

the pseudo-first-order rate constant, were calculated from the slopes of these plots. The buildup and decay of an intermediate species having λ_{max} ~800 nm were analyzed in terms of two consecutive first-order reactions.

In the pH range 7.9 to 10.0 the reduction of $Ru(bipy)_3^{3+}$ was followed on a Cary model 14 spectrophotometer. The decomposition of the complex at lower pH was monitored on a Cary 16. In these runs the solutions were exposed to light only during the intermittent sampling to minimize photolysis of the complex during the rather long time (18 hr) required for complete reaction.

To determine the dioxygen yields, 0.1–2.5 ml of helium-purged ruthenium(III) solution (typically about 0.02 M) was injected into 3.0–7.0 ml of stirred helium-purged buffer or sodium hydroxide contained in a 15 ml capped serum bottle. After 5–20 min, the gas phase above the product solution was sampled and injected onto a 2 m long zeolite column thermostated at 50° and mounted in a Perkin Elmer Vapor Fractometer model 154. Helium was used as carrier gas. Some of the above product solutions and one prepared by slowly adding 500 ml 2×10^{-4} M $Ru(bipy)_3^{3+}$ to an equal volume of 0.02 N NaOH were subjected to ion exchange chromatography on 2 × 15 cm columns of Bio-Rex 70 cation exchange resin (100–200 mesh) in the H^+ form. The columns were eluted with 10^{-3} to 1 N sulfuric acid.

Hydrogen peroxide solutions were prepared by dilution of a 3% solution analyzed by titration with acidic permanganate. The ruthenium(III)-peroxide reaction was followed at 452 nm where plots of $\log(A_\infty - A_t)$ were linear for at least 90% reaction.

RESULTS

The reaction of $Ru(bipy)_3^{3+}$ with water and hydroxide ion

The dioxygen yield exhibits a dramatic pH dependence. The maximum yield (about 80% that predicted from Eq. 2) is obtained at pH 9. The yield drops steeply at both higher and lower pH (5% and 25% at pH 8 and pH 10, respectively) and is essentially negligible at the more extreme pH values (<0.5% below pH 6.8 and 2% at pH 13.6). By contrast, the spectra of the product solutions obtained at pH 4.8, 9.0, and 12.6 are very similar, differing from each other less than 1% in the region of the 452 nm maximum and 5% or less in the region of the 287 nm band. The ion exchange experiments on the reaction mixture formed in 0.02 M NaOH demonstrated the presence of five materials additional to $Ru(bipy)_3^{2+}$. In order of elution, these are: a neutral or anionic species with λ_{max} 265 nm (which is not 2,2′-bipyridine, λ_{max} 280, 230 nm in base and 298, 238 nm in acid); a substance having λ_{max} 645 nm ($\epsilon = 2.6 \times 10^3$ M^{-1} cm^{-1}) and λ_{max} 290 nm ($\epsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}) which accounted for about 2.5% of the ruthenium taken initially; a substance with a slightly modified $Ru(bipy)_3^{2+}$ spectrum; and two higher charged (possibly polymeric) materials which could not be eluted from the column. Parallel ion exchange of 3 mM ruthenium pH 9 and 12.8 product solutions from the dioxygen analyses showed the amount of the 265 nm species to be at least 10 times greater in the latter. Neither solution contained a detectable quantity of the 645 nm component, but both contained small amounts of the higher charged species.

In the 0.01–0.50 M hydroxide range with initial Ru(III) concentrations 5–170 μM, the formation of ruthenium(II) is given by

$$k_{obsd} = k_a[OH^-] + k_b[OH^-]^2 \qquad [3]$$

where $k_a = 148$ M^{-1} sec^{-1} and $k_b = 138$ M^{-2} sec^{-1} at 25°, $\mu = 1.00$ M. The 452 nm rate is largely unaffected by the addition of nucleophiles and radical scavengers: at 0.1 M sodium hydroxide, the rate is 20% slower with 0.5 M added sodium bromide. With 0.1 M *t*-butanol added and 0.1 M sodium hydroxide the rate is the same as in the absence of the alcohol; however at 1.1 M *t*-butanol the 452 nm rate increases by a factor of four. The activation parameters for the k_a path are $\Delta H^\ddagger = 15.3 \pm 1.0$ kcal mol^{-1} and $\Delta S^\ddagger = +7 \pm 3$ cal deg mol^{-1} in the range 6.1 to 35.5° (1 cal = 4.184 J).

In attempting to monitor the disappearance of $Ru(bipy)_3^{3+}$ ($\lambda_{max} = 675$ nm, $\epsilon = 420$ M^{-1} cm^{-1}) an intermediate species, having a broad absorption band in the region 600–850 nm with λ_{max} about 800 nm, was discovered. This species also absorbs strongly in the ultraviolet region; its yield is independent of initial ruthenium(III) concentration ($A_{max}/[Ru(III)]_{initial} \simeq 300$ M^{-1} cm^{-1} at 800 nm and at hydroxide ≥ 0.1 M). Both the formation and the disappearance of this species appear to be first-order processes. As determined from the 800 nm absorbance changes, its formation occurs at essentially the same rate as that of ruthenium(II). Its disappearance is given by $k_{obsd} = 1.2 + 1.1 \times 10^2 [OH^-]$ sec^{-1}. We have found that a very similar species is also generated in the reaction of $Fe(bipy)_3^{3+}$ with hydroxide. The iron intermediate also has λ_{max} near 800 nm. For its formation $k_{obsd}/[OH^-] = 12.8$ M^{-1} sec^{-1}; for its decay $k_{obsd} = 0.2 + 2.8 [OH^-]$ sec^{-1} in the hydroxide range 0.01–0.3 M, at 25° and $\mu = 1.00$ M.

At pH 3 and 4.8 (0.1 M acetate buffer), with initial ruthenium(III) 10–100 μM, the formation of ruthenium(II) follows good first-order kinetics with $k_{obsd} = (1.41 \pm 0.04) \times 10^{-4}$ sec^{-1} ($\mu = 1.00$ M, 25°). In the pH range 7.9–10.0 (0.01 or 0.1 M borate or ammonia buffers) the kinetics are very complicated and the behavior observed depends upon the initial ruthenium(III) concentration.[c] For ruthenium(III) ≥ 1 mM and ≤10 μM the reaction is, however, first order in ruthenium(III) with $k_{obsd} = (2.6 \pm 1.0) \times 10^{-3} + (1.8 \pm 0.5) \times 10^2 [OH^-]$ sec^{-1}.

The reaction of $M(bipy)_3^{2+/3+}$ with hydroxyl radicals

In collaboration with Dr. H. A. Schwarz, the reaction of hydroxyl radical with various tris(bipyridine) complexes was

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[c] As an example, in pH 9.5 borate buffer with initial ruthenium(III) 10 μM, the reaction is first order with $k_{obsd} = 1.40 \times 10^{-2}$ sec^{-1} at 452 nm. The same rate constant is found at 675 nm when ruthenium(III) is 1–2 mM initially, but the reaction rate seems to accelerate after ruthenium(III) declines to about 0.2 mM. When ruthenium(III) is initially ~0.2 mM, the initial (after 10–15 sec) 675 nm absorbance value is about 70% too large, the 675 nm decay is too rapid, and first-order plots of the data are markedly curved, tending to slower rates at longer times. At long times the slopes of the first-order plots approach $k_{obsd} = 1.4 \times 10^{-2}$ sec^{-1}. As such complex observations can be ascribed to interference by impurities, many attempts were made either to determine the nature of or to remove possible impurities: the reaction rate changed 10% or less when iron(III), copper(II), or chromium(VI) was added at the 10^{-5} M level. The same kinetic behavior was observed with ruthenium(III) prepared by lead dioxide, chlorine, or cerium(IV) oxidation. Rates were found to be the same with 0.01 and 0.1 M buffer. It was, however, noted that using aged (>30 min old) ruthenium(III) stock solutions consistently gave too rapid (apparently first-order) reaction. If these observations are indeed indigenous to the $Ru(bipy)_3^{3+}$-hydroxide reaction they can be explained by postulating that a rapidly formed intermediate absorbing strongly at 675 nm confuses the observation of ruthenium(III) disappearance at this wavelength. The detailed time dependence of the absorbance change in these kinetic runs can be simulated in terms of a mechanism invoking product inhibition of the formation of this intermediate.

studied by pulse radiolysis at about 25°. The solutions used were saturated with nitrous oxide and were 10–100 μM in complex [Fe(II), Os(II), and Cr(III) in water; Ru(III) in 0.01–0.001 N acid with μ = 1.00 M, sodium sulfate]. Under all conditions the addition of hydroxyl radical to these complexes was extremely rapid (k_{OH} = (0.6–2.0) × 10^{10} M^{-1} sec^{-1}). Furthermore the reaction yielded *in all instances* a species with an absorption maximum between 750 and 800 nm [ϵ_{max} = (0.5–2.1) × 10^3 M^{-1} cm^{-1}]. The intensity of the 750 nm band for the $Ru(bipy)_3^{2+}$/hydroxyl radical adduct was found to be constant over the pH range 3.6–13.0. Preliminary experiments provide, however, some evidence for a pK at about 13.5. This adduct decayed by second-order kinetics ($2k$ = (1–2) × 10^7 M^{-1} sec^{-1}) over the pH range 5–11. At higher and lower pH the decay was more rapid and followed mixed kinetics which were not very reproducible. By contrast, the disappearance of the $Ru(bipy)_3^{3+}$/hydroxyl radical adduct studied at pH 2–3 was quite slow.

Kinetics of the reaction of $Ru(bipy)_3^{3+}$ with hydrogen peroxide

This reaction was studied at 25° using solutions about 3 μM in $Ru(bipy)_3^{3+}$ (μ = 1.00 M, sodium sulfate). The rate of formation of ruthenium(II), followed at 452 nm, was found to show an inverse acid dependence. For the peroxide reaction two processes must be considered:

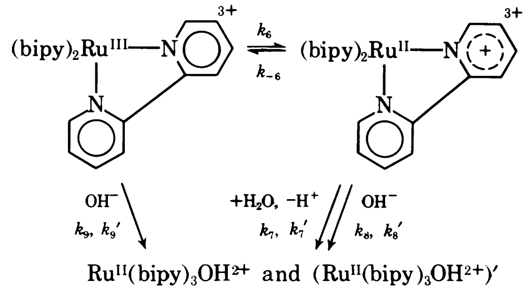
$$Ru(III) + HO_2^- \text{ (or } H_2O_2) \xrightarrow[OH^-]{k_4} Ru(II) + O_2^- \text{ (or } HO_2) \quad [4]$$

$$Ru(III) + O_2^- \text{ (or } HO_2) \xrightarrow{k_5} Ru(II) + O_2 \quad [5]$$

Such a sequence may lead to complex kinetic behavior (8), but yields a single exponential for formation of ruthenium(II) when $k_5\,[O_2^-] \gg k_4\,[H_2O_2]$. Under these conditions $k_{obsd}/[H_2O_2] = 2k_4$. Thus we report here only values for $k_{obsd}/2[H_2O_2]$ determined from the low peroxide region. Values for this ratio are as follows: in 2 × 10^{-3} N H_2SO_4, 4.2 M^{-1} sec^{-1}; in 0.01 M Tris buffer, pH 8.40, 1.64 × 10^4 M^{-1} sec^{-1}; in 0.01 M ammonia buffer at pH 9.66, 2.54 × 10^5 M^{-1} sec^{-1}. The pH dependence of $k_{obsd}/[H_2O_2]$ is consistent with a scheme in which HO_2^- is the reactive reducing agent in the alkaline pH range. Using pK_W = 13.8 (9) and $pK_{H_2O_2}$ = 11.67 (10), values of 2.7 × 10^7 M^{-1} sec^{-1} and 4.2 M^{-1} sec^{-1} are obtained for $k_{HO_2^-}$ and $k_{H_2O_2}$, respectively. The reaction of hydrogen peroxide with a 10% excess of ruthenium(III) at pH 6.8 and in 1.0 N sulfuric acid yields 83 ± 15% as much dioxygen as is produced from reaction of the same quantity of hydrogen peroxide with excess cerium(IV) sulfate.

DISCUSSION

For reaction of $Ru(bipy)_3^{3+}$ with water or hydroxide ion, the kinetic studies implicate pathways zero-, first-, and second-order with respect to hydroxide ion. Below pH about 7 the hydroxide-independent path predominates while above pH 13 the second-order hydroxide path makes a substantial contribution. The latter could arise from the attack of hydroxide on a ruthenium(III)-hydroxide ion pair or could be caused by the change in medium. It will not be discussed further. The dioxygen yield is maximal in a pH range where the kinetics are complex but the first-order hydroxide path predominates. The steep drop in yield at higher base concentrations does not coincide with a change in the rate-determining step for the reaction. Over the entire pH range the formation of $Ru(bipy)_3^{2+}$ remains predominantly first-order in character. Moreover the absence of any effect of added bromide and *t*-butanol shows that free hydroxyl radicals (or the conjugate base O^-) are not produced in the reaction. These and other observations are embodied in the following scheme (Eqs. **6–9**).



Reaction **6**, the rate-determining step for the low pH reaction, is an intramolecular electron-transfer from a bound bipyridine in $Ru(bipy)_3^{3+}$ to the metal center. The carbonium-ion-like radical generated in Eq. **6** may either return spontaneously to the starting complex or react with water (Eq. **7**) or hydroxide ion (Eq. **8**). Eq. **9**, direct attack of hydroxide on $Ru(bipy)_3^{3+}$, corresponds to the rate-determining step for the first-order hydroxide term in the high pH rate law (Eq. **3**). The products of Eqs. **7–9** are isomeric and the proportions of the two formed by the three pathways are not necessarily the same. In the presence of excess $Ru(bipy)_3^{3+}$, $Ru(bipy)_3OH^{2+}$, and $(Ru(bipy)_3OH^{2+})'$ are rapidly oxidized to $Ru(bipy)_3OH^{3+}$ and $(Ru(bipy)_3OH^{3+})'$, respectively (Eq. **10**).

$$Ru(bipy)_3^{3+} + Ru^{II}(bipy)_3OH^{2+} \text{ or } (Ru^{II}(bipy)_3OH^{2+})' \xrightarrow[\text{fast}]{k_{10},\, k_{10}'} Ru(bipy)_3^{2+} + Ru^{III}(bipy)_3OH^{3+} \text{ or } (Ru^{III}(bipy)_3OH^{3+})' \quad [10]$$

Subsequent reactions of these species to yield dioxygen and other products are discussed later. Applying the steady-state approximation for the concentration of the ruthenium(II) intermediates gives

$$-\frac{d[Ru(III)]}{dt} = 2\left\{\left(\frac{(k_7 + k_7') + (k_8 + k_8')[OH^-]}{k_{-6} + (k_7 + k_7') + (k_8 + k_8')[OH^-]}\right)k_6 + (k_9 + k_9')[OH^-]\right\}[Ru(III)]$$

From this scheme, the rate constant measured at pH 3–4.8 is $2\,k_6/(k_{-6} + k_7 + k_7')$ = (1.41 ± 0.04) × 10^{-4} sec^{-1}, while the intercept obtained by extrapolation of the intermediate (pH 7.9–10.0) pH data for high and low ruthenium(III) is $2k_6$ = (2.6 ± 1.0) × 10^{-3} sec^{-1}. Further, for the first-order hydroxide term in the rate law Eq. **3**, $k_a = 2(k_9 + k_9')$ = 1.48 × 10^2 M^{-1} sec^{-1}.

We propose that the intermediates formed in Eqs. **7–9** result from nucleophilic addition of hydroxide to the ligand[d]

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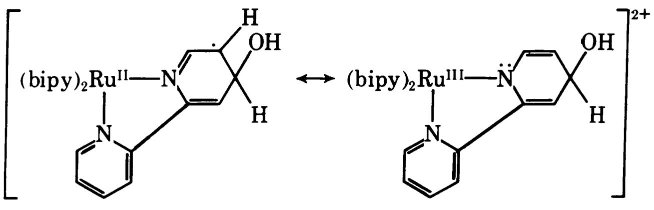
[d] A related mechanism has been proposed for the $Fe(bipy)_3^{3+}$/hydroxide reaction [G. Nord and O. Wernberg, personal communication (1974)].

to yield, e.g., **Ia–b** when addition is to the 4-position. Hydroxide or water additions to N-heterocycles analogous to Eq. 9 are well known for purely organic systems (11, 12). The proposed structure **Ia–b** is the same as that expected for the species resulting from 4-addition of hydroxyl radical to $Ru(bipy)_3^{2+}$. That hydroxide addition to a bipyridyl ring occurs in the $Ru(bipy)_3^{3+}$/hydroxide reaction is supported by the fact that the intermediate observed in the stopped-flow studies has an absorption maximum in the same region (750–800 nm) as the species resulting from hydroxyl radical addition to $M(bipy)_3^{2+/3+}$. The 800 nm absorbing stopped-flow intermediate cannot, however, be identical with the pulse radiolysis $Ru(bipy)_3^{2+}$/hydroxyl adduct because its decay rate is much too slow. Rather it is most likely a ruthenium(III) species formed in the outer-sphere oxidation Eq. **10**. This hypothesis is appealing since the pulse radiolysis studies demonstrated a relatively slow decay of the $Ru(bipy)_3^{3+}$/hydroxyl adduct. Two isomeric ruthenium(III) products are then required in Eq. **10** because the 800 nm intermediate cannot carry the bulk of the $Ru(bipy)_3^{3+}$/hydroxide reaction; this species attains its maximum concentration when ruthenium(II) production is ~90% complete. In the present scheme, the two isomers originate from hydroxide addition to different positions of bipyridine bound to ruthenium(III) (Eq. **9**). If $(Ru(bipy)_3OH^{3+})'$ denotes the 800 nm absorbing stopped-flow intermediate, then $k_9' < k_9$ and reaction 10,10′ must be quite rapid. It is worth noting that both nucleophilic attack of hydroxide on $Ru(bipy)_3^{3+}$ and electrophilic addition of hydroxyl radical to $Ru(bipy)_3^{2+}$ should occur preferentially at the 4- and 6-positions of bipyridine. Consequently, either or both of the products of Eq. **9** may be identical with the adduct(s) formed from pulse radiolysis of $Ru(bipy)_3^{2+}$.



Ia **Ib**

One of the most remarkable features of the $Ru(bipy)_3^{3+}$/hydroxide reaction, the steep dependence of dioxygen yield upon pH, finds no ready explanation in terms of the pulse radiolysis studies of the $Ru(bipy)_3^{2+}$/hydroxyl reaction at various pH values. There is no spectrophotometric evidence for pH-dependent equilibria over the pH range 3.6–13.0; furthermore, the second-order rate constant for the decay of the adduct remains nearly constant throughout this range. As pH-dependent reactions of the $Ru(bipy)_3OH^{2+}$ adducts must be neglected, base-dependent reactions of the $Ru(bipy)_3OH^{3+}$ species are invoked to account for the pH dependence of the product distribution. In Eqs. **11–13** these are shown for only one isomer for the sake of brevity.

$$Ru(bipy)_3OH^{3+} \underset{\text{fast}}{\overset{K_{11}}{\rightleftharpoons}} Ru(bipy)_3O^{2+} + H^+ \quad [11]$$

$$Ru(bipy)_3O^{2+} \underset{\text{slow}}{\xrightarrow{OH^-}} Ru(bipy)_3^{2+} + HO_2^- \quad [12]$$

$$Ru(bipy)_3OH^{3+} + Ru(bipy)_3O^{2+} \longrightarrow 2Ru(bipy)_3^{2+} + O_2 + H^+ \quad [13]$$

Uni- or bimolecular decomposition of $Ru(bipy)_3OH^{3+}$ or $(Ru(bipy)_3OH^{3+})'$ at low pH culminates in degradation of the ligand with no net water oxidation.[e] Similarly, at high pH decomposition of $Ru(bipy)_3O^{2+}$ or $(Ru(bipy)_3O^{2+})'$ effects ligand degradation, for the most part, but some peroxide (Eq. **12**) results. Peroxide formed in Eq. **12** is oxidized by $Ru(bipy)_3^{3+}$ (Eqs. **4** and **5**) to form dioxygen. Such a sequence (Eqs. **12, 4,** and **5**) is reasonable in view of the report by Dwyer and Gyarfas (13) that hydrogen peroxide is detectable in systems of this kind. Eq. **12** accounts for the small residual (about 2%) yield of dioxygen at high pH. The bulk of the dioxygen is, however, formed directly by Eq. **13**. As this reaction is expected to contribute substantially to dioxygen production only over the pH range where both $Ru(bipy)_3OH^{3+}$ or $(Ru(bipy)_3OH^{3+})'$ and their conjugate base forms have comparable concentrations, K_{11} must be about 10^{-9} M. Further evidence for the intervention of reactions such as Eq. **13** that are second-order in ruthenium(III) is provided by the behavior of the chemiluminescence [Creutz and Sutin, unpublished results (1974)].

The above mechanism, although not implausible, is by no means unique. Not all features of the reaction are understood; nevertheless, the combined evidence from the kinetic, product, and pulse radiolysis studies strongly implies that dioxygen formation results from reaction of species in which hydroxide has been added to the bound bipyridine ring. Such reactions lead to the equivalent of those of free hydroxyl (but avoid its thermodynamically expensive formation), and the $Ru(bipy)_3$ moiety may be said to chaperone hydroxyl through the reaction sequence.

A solar energy storage system

Upon absorption of light in the visible region, $Ru(bipy)_3^{2+}$ yields $^*Ru(bipy)_3^{2+}$ which is, in principle, capable of reducing water or hydrogen ion to dihydrogen in the pH range 0–14 (1). As shown in this study, the $Ru(bipy)_3^{3+}$ produced in the dihydrogen-generating reaction can be rapidly reduced by hydroxide with the liberation of dioxygen. The tris(bipyridine)ruthenium and related systems may by this means effect the photodecomposition of water into its elements. This photodecomposition, with the accompanying separation of the dihydrogen and dioxygen produced, might be accomplished in a cell of the following type. An *n*-type semiconductor electrode (14, 15) is connected to a metal electrode, e.g., platinum, and the two electrodes are immersed in a pH 9 buffer containing $Ru(bipy)_3^{2+}$. The semiconductor electrode is illuminated and the $^*Ru(bipy)_3^{2+}$

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[e] Dimerization reaction(s) of the $Ru(bipy)_3OH^{2+}$ species probably occur to some extent and may account for the higher charged fraction found in the ion exchange experiments. The parallel of such reactions has been observed for hydroxycyclohexadienyl radicals (Walling, C. & Johnson, R. A. (1975) *J. Am. Chem. Soc.* **97**, 363–367). One possible side reaction is the decomposition of $Ru(bipy)_3OH^{3+}$ to a ruthenium(II) pyridone. Another of the products of the hydroxide reaction probably results from ligand loss to give ultimately $[Ru^{III}(bipy)_2OH_2]_2O^{4+}$. This is suggested by the similarity of the spectrum of the 645, 290 nm absorbing product to the spectra of compounds of this type (Weaver, T. R., Meyer, T. J., Adeyemi, S. A., Brown, G. M., Eckberg, R. P., Hatfield, W. E., Johnson, E. C., Murray, R. W. & Untereker, D. (1975) *J. Am. Chem. Soc.* **97**, 3039–3048).

near the electrode surface injects an electron into the conduction band of the semiconductor.[f] The $Ru(bipy)_3^{3+}$ resulting is then reduced by hydroxide ion to the starting complex with the production of dioxygen. The electrons released by the $^*Ru(bipy)_3^{2+}$ flow from the semiconductor electrode through the external circuit to the platinum electrode where they effect the reduction of water (or hydrogen ion) to dihydrogen. The net reaction occurring in the cell would thus be the photodecomposition of water into dihydrogen and dioxygen.

The advantage of this type of cell over others described previously would be that a substrate photochemically active in the visible region of the spectrum can be rapidly regenerated by oxidation of water. Previously described cells have either not functioned by the absorption of light in the visible region (14, 15) or have required the addition of a reducing agent to regenerate the photosensitizer (16–19). Finally, these studies also suggest the use of catalytic amounts of $Ru(bipy)_3^{2+}$ [or perhaps a related complex like the less costly $Fe(bipy)_3^{2+}$] to regenerate a reduced photosensitizer in "dark" reactions. The $M(bipy)_3^{3+}$, etc. produced would then yield dioxygen and reform $M(bipy)_3^{2+}$ upon subsequent reaction with hydroxide.

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1. Navon, G. & Sutin, N. (1974) *Inorg. Chem.* **13**, 2159–2164.
2. Demas, J. N. & Crosby, G. A. (1971) *J. Am. Chem. Soc.* **93**, 2841–2847.
3. Harrigan, R. W., Hager, G. D. & Crosby, G. A. (1973) *Chem. Phys. Lett.* **21**, 487–490.
4. Hercules, D. M. & Lytle, F. E. (1966) *J. Am. Chem. Soc.* **88**, 4745–4746.
5. Lytle, F. E. & Hercules, D. M. (1971) *Photochem. Photobiol.* **13**, 123–133.
6. Nord, G. & Wernberg, O. (1972) *J. Chem. Soc., Dalton*, 866–868.
7. Buckingham, D. A. & Sargeson (1964) in *Chelating Agents and Metal Chelates*, eds. Dwyer, F. P. & Mellor, D. P. (Academic Press, New York), pp. 269–280.
8. Frost, A. G. & Pearson, R. G. (1961) in *Kinetics and Mechanism* (Wiley, New York), 2nd ed., p. 178.
9. Sillén, L. G. & Martell, A. E. (1964) "Stability Constants of Metal-Ion Complexes," *Special Publication No. 17* (The Chemical Society, London), p. 40.
10. Evans, M. G. & Uri, N. (1949) *Trans. Faraday Soc.* **45**, 224–230.
11. Albert, A. (1967) *Angew. Chem. Int. Ed. Engl.* **6**, 919–928.
12. Bunting, J. W. & Meathrel, W. G. (1973) *Can. J. Chem.* **51**, 1965–1972.
13. Dwyer, F. P. & Gyarfas, E. C. (1952) *J. Am. Chem. Soc.* **74**, 4699–4700.
14. Fujishima, A. & Honda, K. (1972) *Nature* **238**, 37–38.
15. Wrighton, M. S., Ginley, D. S., Wolczanski, P. T., Ellis, A. B., Morse, D. L. & Linz, A. (1975) *Proc. Nat. Acad. Sci. USA* **72**, 1518–1522.
16. Tributsch, H. & Calvin, M. (1971) *Photochem. Photobiol.* **14**, 95–112.
17. Gerischer, H. (1972) *Photochem. Photobiol.* **16**, 243–260.
18. Honda, K. (1974) in *The Current State of Knowledge of Photochemical Formation of Fuel*, ed. Lichtin, N. N. (report of an NSF-RANN sponsored workshop held at North Andover, Mass. on Sept. 23 and 24, 1974), pp. 22–23.
19. Wang, J. H. (1969) *Proc. Nat. Acad. Sci. USA* **62**, 653–660.

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[f] A semiconductor electrode is desirable for this purpose because of its "rectifying" properties and may be required since metal electrodes are likely to quench $^*Ru(bipy)_3^{2+}$ with regeneration of $Ru(bipy)_3^{2+}$ and the production of heat. It should be noted, however, that the role of the semiconductor electrode in this cell is not the same as in the Fujishima-Honda cell (14). In the latter cell, electrons are excited from the valence to the conduction band of the semiconductor by absorption of light, while in the cell proposed here the light is absorbed by $Ru(bipy)_3^{2+}$ and an electron from $^*Ru(bipy)_3^{2+}$ is injected into the conduction band of the semiconductor. The restriction imposed by the short lifetime of $^*Ru(bipy)_3^{2+}$ might be partially overcome by coating the electrode with ruthenium(II) or by use of an optically transparent electrode.