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**R. Marshall Wilson,* John W. Rekers**
*Department of Chemistry, University of Cincinnati*
*Cincinnati, Ohio 45221*

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## Applications of Light-Induced Electron-Transfer Reactions. Coupling of Hydrogen Generation with Photoreduction of Ruthenium(II) Complexes by Triethylamine

*Sir:*

The photoinduced splitting of water to hydrogen and oxygen using visible or near-UV light continues to be the subject of intensive investigation.[1-9] Potential light-absorbing catalysts that have been particularly well-studied include chlorophyll,[1] several dyes and transition metal complexes such as tris(2,2′-bipyridine)ruthenium(II) (**1**), and related compounds.[5-9] Very recently it has been shown that several one-electron oxidizing or reducing agents can be coupled to produce the oxidation or reduction, respectively, of water through the use of heterogeneous catalysts such as $PtO_2$ or $IrO_2$[6,8,10-12] or in photoelectrochemical cells.[13] Previously we found that certain hydrophobic ruthenium(II) complexes can be photoreduced efficiently by amines using visible light in nonaqueous solution.[14] In the present paper we report the coupling of this reaction with the reduction of water in a net process leading to hydrogen evolution in good quantum efficiency with a high turnover in terms of moles of hydrogen produced/mole of light-absorbing metal complex.

Although many light-induced electron-transfer reactions result in no net chemistry due to energy-wasting back electron transfer,[15] we recently found that for some hydrophobic ruthenium(II) complexes such as **2** ($RuL_3^{2+}$, where L = 4,4′-dicarboxy-2,2′-bipyridine diisopropyl ester) photolysis in the presence of certain oxidants[16,17] or reductants[14] in nonaqueous solutions can lead to the isolation of one of the primary one-electron transfer products. Thus, irradiation of **2** with visible light in dry acetonitrile containing triethylamine leads to a net photoreduction of **2** with a quantum efficiency, $\phi \simeq 0.4$ (eq 1):[14]

$$2RuL_3^{2+} + 2Et_3N \xrightarrow[\sim 500\ \mathrm{nm}]{h\nu} 2RuL_3^{+} + Et_3NH^{+} + Et_2N^{+}{=}CHCH_3 \quad (1)$$

When the reaction is carried out in the presence of water, acetaldehyde is formed as a product,[18] but there is no accumulation of the reduced metal complex, $RuL_3^+$. The involvement of water evidently occurs after the excited-state quenching process, since water does not quench the luminescence of **2** but has been found to react rapidly with $RuL_3^+$ in acetonitrile.[14] The details of the interaction between water and $RuL_3^+$ are currently under investigation. Prolonged irradiation of **2** in aqueous acetonitrile containing triethylamine leads to a slow decomposition of the metal complex.

We now find that irradiation of solutions containing **1** or **2** in the presence of a small amount of Adams' catalyst ($PtO_2$) results in a net photostability of the metal complex with a steady evolution of hydrogen gas. In typical experiments an argon deaerated solution of **2** ($6 \times 10^{-5}$ M) in acetonitrile with 0.3 M triethylamine and 25% water was stirred with ca. 5 mg of $PtO_2$ and irradiated with visible light.[19] The gas above the solution was analyzed by gas chromatography and mass spectrometry; the major product formed during several hours irradiation was found to be hydrogen.[19] Replacement of water with deuterium oxide led to the production of $D_2$; comparison of the isotopic distribution resulting from the photolysis (by mass spectrometry) with that produced by electrolysis of a sample of the same $D_2O$ indicated that water is the source of the hydrogen produced in the photolysis. Experiments omitting separately the light, $PtO_2$, triethylamine, ruthenium complex, and water all resulted in no generation of hydrogen. The quantum yield for hydrogen production using monochromatic 436-nm light from a 1000-W mercury-xenon lamp was determined to be 0.3;[20] a turnover number of 300 mol of $H_2$ per mol of **2** was obtained for moderate irradiation periods in which the hydrogen was allowed to collect above the stirred solution. Prolonged irradiation of stirred solutions leads to a slow decrease in the content of hydrogen in the volume above the solution; presumably this is caused by a $PtO_2$-catalyzed reaction with unsaturated products generated in the photolysis. Experiments with **1** led to similar results; with the same amount of catalyst present, a quantum yield of 0.37 was obtained at 436 nm.[20]

The results are most consistent with a mechanism (eq 2-6) in which photochemically generated $RuL_3^+$ reacts with a source of protons (water in the net sense) in the presence of $PtO_2$ to give $RuL_3^{2+}$ and $H_2$. However, the neutral radical **3** is also a strong reducing agent,[21,22] and in the absence of reaction 4 (which may be unfavorable for **1**) it may be directly involved in the generation of $H_2$ (e.g., eq 6). Since we also observe oxidation of $RuL_3^+$ produced by irradiation of **2** in the presence of $NEt_3$ and $PtO_2$ when water is excluded (eq 7), it is unclear whether $RuL_3^+$ reacts first with water and then with $PtO_2$, or whether $RuL_3^+$ acts as a simple electron-transfer carrier (eq 7). The relatively high quantum efficiencies obtained are noteworthy, since the stoichiometry indicated by eq 2-5 suggests that $\phi_{max}$ for the production of $RuL_3^+$ should be twice that for hydrogen evolution. The higher than expected value may reflect a higher initial yield of free ions in the more polar aqueous acetonitrile mixture, since our studies have indicated lower efficiencies for reduction in nonpolar solvents.[14]

$$RuL_3^{2+*} + Et_3N{:} \rightarrow RuL_3^{+} + Et_3N^{+}\cdot \quad (2)$$

$$Et_3N^{+}\cdot + Et_3N{:} \rightarrow Et_3NH^{+} + \underset{\mathbf{3}}{CH_3\dot{C}H\text{-}NEt_2} \quad (3)$$

$$\mathbf{3} + RuL_3^{2+} \rightarrow RuL_3^{+} + CH_3{=}NEt_2^{+} \quad (4)$$

$$2RuL_3^+ + 2H^+ \xrightarrow{PtO_2} 2RuL_3^{2+} + H_2 \tag{5}$$

$$23 + 2H^+ \xrightarrow{PtO_2} 2CH_3CH{=}NEt_2^+ + H_2 \tag{6}$$

$$RuL_3^+ + PtO_2 \rightarrow RuL_3^{2+} + \text{“}PtO_2^-\text{”} \tag{7}$$

The results reported here appear somewhat related to those obtained by Lehn and Sauvage[6] and by Kalyanasundarum et al.[8] and others,[9,10] where irradiation of metal complexes in the presence of platinum catalyst systems and other reagents also leads to hydrogen production. However, the present results involve a much simpler system and a high quantum efficiency. It is particularly noteworthy that in this case the primary photoproduct $RuL_3^+$ is directly and efficiently coupled to water reduction. Like the other systems, the present results involve water reduction at the expense of an external reductant, in this case triethylamine. Thermochemical data[23] indicate that the overall reaction (eq 8) is moderately endothermic ($\Delta H \simeq$ 14 kcal/mol). We are currently extending our studies using other metal complexes in which ligand modification affords both proton binding sites and a more favorable reduction potential, so that milder reducing agents can be used.

$$Et_3N + H_2O \xrightarrow[RuL_3^{2+}\ \text{visible light}]{\qquad\qquad} Et_2NH + CH_3CHO + H_2 \tag{8}$$

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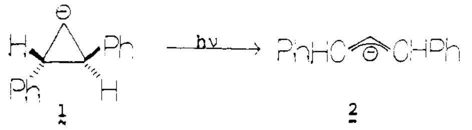
**Patricia J. DeLaive, B. P. Sullivan**
**T. J. Meyer, D. G. Whitten***
*Department of Chemistry, University of North Carolina*
*Chapel Hill, North Carolina 27514*

*Received February 22, 1979*

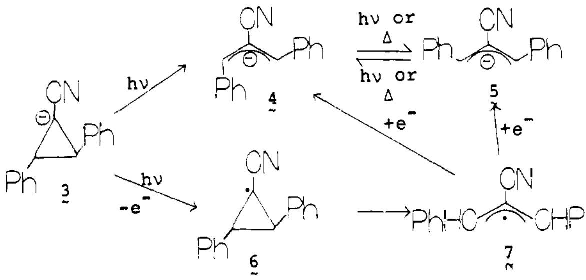
## Orbital Topology in a Photochemical Carbanionic Ring Opening

*Sir:*

Although orbital topological control in thermal pericyclic reactions of carbanions has been amply demonstrated,[1] its importance in photochemical carbanionic ring openings remains uncertain.[2] The symmetry-predicted disrotatory excited-state opening of trans-2,3-disubstituted cyclopropyl to allyl anions, e.g., **1** to **2**,[3] should potentially provide convenient systems for further study since the expected product should convert, by analogy to the 1,3-diphenylpropenyl anion **2**, only slowly into its geometric isomer if the photolysis is conducted at sufficiently low temperatures.[4-6]



Thus, the production of a nonequimolar mixture of *cis*- and *trans*-α-benzylcinnamonitrile upon low-temperature proton quench of the photochemically ring-opened product derived from **3** has several possible interpretations. Among these are (1) a symmetry-controlled disrotatory opening to **4**, the expected *E,Z* isomer, followed by thermal geometric equilibration, possibly during protonation;[5] (2) a photoinduced cis–trans isomerization (**4** ⇌ **5**), a known process for **2**;[6] (3) a photoinduced electron ejection from **3** to form the corresponding radical **6** which could open[7,8] to the ultimately stereorandom[8] allyl radical **7** before recapturing an electron to form a mixture of **4** and **5**; or (4) an absence of orbital symmetry direction of the ring opening. A reexamination of this reaction originally studied by Newcomb and Ford[3] suggests that, in the absence of complicating secondary reactions, the disrotatory mode predicted by orbital symmetry can be observed, possibly by two primary photochemical pathways.



Upon irradiation with a Pyrex-filtered 450-W medium-pressure mercury lamp, a solution of **3**[3] ($5 \times 10^{-3}$ M) in THF-$d_8$ (generated by treating *cis,trans*-2,3-diphenylcyclopropanecarbonitrile with lithium diisopropylamide) at −70 °C became bright red, indicating the formation of **4** and/or

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