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VISIBLE LIGHT INDUCED ELECTRON TRANSFER REACTIONS OF METAL COMPLEXES. PRODUCTION OF HYDROGEN FROM WATER BY A $Ru(bpy)_3^{2+}$-$Fe_4S_4(SBzl)_4^{2-}$ SYSTEM

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Hydrogen is generated without addition of extra electron donor when aqueous solution of $Ru(bpy)_3^{2+}$ and synthetic iron-sulfur complex, $Fe_4S_4(SBzl)_4^{2-}$, is illuminated by a "sunlight lamp". Result shows that the Fe-S chelate plays an important role, presumably as an electron carrier. Probable mechanism is also presented.

As is well recognized, the photoredox decomposition of water into its elements continues to receive increasing attention as a viable means of solar energy conversion and storage.1) Tris(2,2'-bipyridine)ruthenium(II) complex has been particularly extensively studied, and turned out to be one of the most attractive photosensitizers for this purpose.2) Generation of hydrogen and oxygen is actually observed in several laboratories with this photocatalyst. However, substantially all the systems so far examined are sacrificial ones, and need extra additives such as electron donor3) or acceptor4-5) other than water itself. One exception may be the current finding from Grätzel's laboratory, namely they reported that cyclic water cleavage was achieved through combination of two types of catalyst.5-6)

We have been interested in roles of iron-sulfur proteins in living organisms, especially the ones in photosystem I of plant photosynthesis and hydrogenases. Studies on synthetic analogues of the active site of the proteins have been intensively carried out by Holm and his coworkers.7) And in recent years, it has been possible to utilize such man-made Fe-S species in organic synthesis as well as simulating reactions *in vivo*.8) Consequently, using $Ru(bpy)_3^{2+}$- and $Fe_4S_4(SBzl)_4^{2-}$-chelates, we have examined a photoinduced reduction of water whereby molecular hydrogen is generated. This paper deals with the first successful result of water reduction by such a new system as in the title.

The investigated basic system consists of a mixture containing dimethylacetamide(5 ml), aqueous acetate(M/10) or phosphate(M/15) buffer(15 ml), $Ru(bpy)_3Cl_2\cdot 6H_2O$, (abb. Ru^{2+}), and $[Fe_4S_4(SBzl)_4]$-$(Et_4N)_2$, (abb. t^{2-}).9-10) The solution in a Pyrex flask was illuminated under argon with a 400-W "sunlight lamp" (Toshiba D400 or DR400). Production of hydrogen was followed as a function of time by gas chromatographic analysis (molecular sieves 13X at 35°), and confirmed by mass spectrometry too in some cases.

Results are shown in Fig. 1 and Table. Included as well in Table for comparison are rates of hydrogen formation (r value; μl/day/liter solution) determined from the initial slopes.

At the outset of this study experiments in the presence of an electron donor (EDTA) were performed in order to evaluate this system, and the data obtained are comprized in Table (runs 1-4).

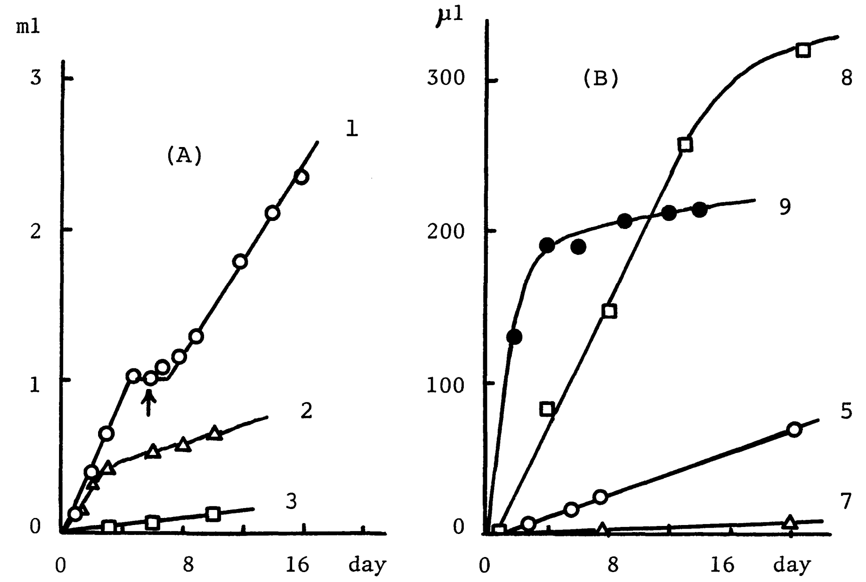


Fig. 1. Hydrogen generation as a function of time.

(A) Effect of $Fe_4S_4(SBzl)_4^{2-}$ in the presence of EDTA; ratio of t^{2-}/Ru^{2+} is 1, 0.1 and 0 for 1, 2 and 3, respectively; Additional introducing of t^{2-} is indicated by the arrow. See text.

(B) H_2 formation in the absence of EDTA; 5(pH=5), 7(pH=9)--- without platinum catalyst; 8(1mM of Ru^{2+}), 9(0.1mM 0f Ru^{2+})--- with Pt catalyst: See the table for further details; the numbers employed here correspond to those of run.

Fig. 1-A shows clearly that the Fe-S complex plays an important role in this device. Higher yield of hydrogen was obtained with increasing the ratio of t^{2-}/Ru^{2+} (runs 1-2). Both r and turnover of Ru^{2+} values in 1 where the ratio was unity were twenty times greater than those of 3 in which it was zero. If the reaction proceeds ideally, viz., both t^{2-} and Ru^{2+} act as stable catalysts, linear slope of the H_2 production vs. time should be expected. A marked decrease of the rate in 2 after around three days may be explained in terms of disintegration of t^{2-}, since Ru^{2+} is recognized to be more stable than the Fe-S complex in an acidic medium and to oxygen. This explanation can be also supported by resultant recovery of the rate in 1 after the second addition of t^{2-} (indicated by arrow in Fig. 1-A), and by linear relationship in 3 where no Fe-S chelate was introduced.

Even if the stability of the catalyst seems to be a problem, this system has, nevertheless, proved of great value. And our next attention was then focused on splitting water itself, that is, reactions in the absence of extra electron donor. Experiments excluded EDTA and platinum catalyst were carried out as exploratoly work. We have found that hydrogen generation was really observed even in such conditions (Fig. 1-B & runs 5-7 in Table).11) And a remarkable pH dependence was seen; the values of r were 184, 38 and 16 at pH 5, 7 and 9, respectively.

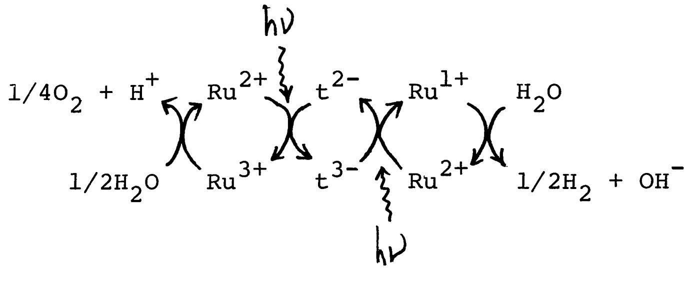
TABLE Hydrogen generation by visible light irradiation of the $Ru(bpy)_3^{2+}/Fe_4S_4(SBzl)_4^{2-}$ system.

Run	Ru^{2+} mM	t^{2-} μM	pH	EDTA mM	K_2PtCl_6 mM	Total volume of H_2 evolved in μl[a] (day irradiated[b])	Turnover value[c] Ru^{2+}	Turnover value[c] t^{2-}	Rate of H_2 formation (r)[e] (μl/d/l soln)
1	0.1	100	4.1	100	0.61	2351 (15.7)	105	53[d]	11300
2	0.1	10	4.1	100	0.59	643 (10.0)	29	287	8450
3	0.1	-	4.2	100	0.55	117 (10.0)	5	-	550
4	1.0	100	5.0	30	-	93 (17.8)	0.4	4	262
5	0.75	76	5.1	-	-	69 (20.4)	0.4	4	184
6	0.75	76	7.1	-	-	10 (20.4)	0.06	0.6	38
7	0.75	76	8.9	-	-	6 (20.4)	0.04	0.4	16
8	1.0	100	5.1	-	0.47	319 (20.8)	1.4	14	1015
9	0.1	100	4.9	-	0.50	215 (14.0)	9.6	9.6	3275

(a) per 20 ml of solution (b) D400 lamp (10 cm from the surface) for runs 1-4; DR400 (15 cm distance) for 5-9. (c) calculated as two electrons per H_2 molecule (d) Total concentration of 0.2 mM was employed. See text. (e) Determined from initial slope.

This result is particularly important in view of the fact that water itself must have acted as both electron donor and acceptor, since no extra additives such as EDTA or triethanolamine had been introduced into the solution. A preliminary reaction conducted in deuterium oxide (93 atom % D; equivalent to 86.8 atom % D for molecular hydrogen) yielded H_2 gas (r=54 μl/d/l soln) which was shown by mass spectrometry to consist of 60%D_2, 32%HD and 8%H_2. The D content obtained was about 10 % lower than the anticipated, but it may be safe to say that at some stage protons from water are involved, making the present system a photochemical water reduction process. The probable role of this synthetic iron-sulfur specimen as an electron carrier[12)] is specially noteworthy in connection with a hitherto recognized one in nature. We should point out that yield of hydrogen was greatly enhanced by the use of platinum catalyst (runs 8-9). This may lead to a solution letting this system be more efficient and practically useful by employing other modifications of the catalyst.[13)] Fig. 1-B illustrates typical results mentioned above.

The following scheme appears to be one of the plausible representations. Induction periods are discernible in 5, 7 and 8, at least approximately, from the figure 1-B. This might involve transformation of t^{2-} into t^{3-},[14)] presumably by excited Ru^{2+} ($Ru^{3+}/{*Ru^{2+}}$=-0.84V vs.



NHE),15) supporting our proposed mechanism where t^{3-} serves as an electron carrier. This explanation may be also substantiated by the fact that no lag period was seen in the presence of EDTA. Since this is considered to possess enough redox potential16) for reducing t^{2-},14) and/or makes the electron transport reaction become more favorable (see Fig. 1-A). It is not probable that unstable t^{1-},7b) plays an important part, since maximum value of about 300 is so far obtained as the turnover number of t^{2-} (run 2). We have not yet succeeded in observing simultaneous evolution of oxygen with unhydrated RuO_2.17) However , from studies of model system,4) we have the evidence that reduction of $Co^{III}(NH_3)_5Cl\cdot Cl_2$ does occur.17) Recently, it is reported that hydrated RuO_2 worked, but the unhydrated one failed to give oxygen.5) Thus we believe it will be possible to generate hydrogen and oxygen from water simultaneously by employing the soluble form of RuO_2 in our present system. The related work is currently actively underway as well as detailed mechanistic investigations, and will be discussed elsewhere.

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10) Our preliminary experiments were carried out with the SBu-t derivative which was given to one of us (Y. Okuno) by Professor R. H. Holm, and we are indebted to him for the gift and his encouragement.
11) Slower reaction was observed (r=70, turnover=0.09), when t^{2-} was omitted.
12) Practically no H_2 was produced by irradiation of the solution without Ru^{2+}, though small amount of H_2 was seen by glc (8 µl from 20 ml of solution after 11 day irradiation).
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17) The fate of oxidation site was not pursued further. Production of OH· may be plausible.

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