

Kinetic Investigations of New Viologen Derivatives for Water Photolysis. The First Relay Compound with Stable Radicals

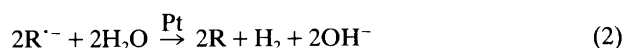
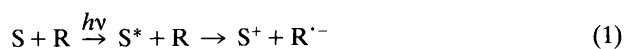
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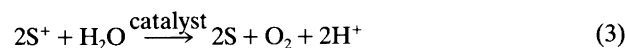
Six new electron relay compounds for the transfer of electrons from excited dyes [e.g. tris(2,2'-bipyridyl)ruthenium(II) chloride, Ru(bipy)₃²⁺*] to catalysts (e.g. colloidal Pt) in aqueous photolytical systems were studied. The discharging rate constants of the radicals on different platinum catalysts were measured. The hydrogen production rates and quantum yields of systems with Ru(bipy)₃²⁺, electron relay, EDTA and Pt were determined. The stability of 1,1'',1'''-trimethyl[4,2';4',4'';6',4''']quaterpyridinium trichloride, against oxygen, was much higher than that of methyl viologen and its derivatives. With this relay compound hydrogen production was achieved even in the presence of dissolved oxygen. The quantum yields (400 < λ < 500 nm) were between 1 and 26 %. The absorption coefficients of the electron relay radicals were measured.

Redox reactions driven by visible light have attracted wide attention in recent years. In aqueous solution an electron relay compound (R) receives on one or more electrons from an excited dyestuff [the sensitizer, denoted by S in reaction (1)] and transports them to a colloidal platinum catalyst for water reduction [reaction (2)]. An important group of electron relay compounds are the viologens, formally known as 1,1'-disubstituted 4,4'-bipyridinium salts.¹



The fact that systems containing hydrogen and colloidal platinum are able to hydrogenate the double bonds of the viologens is one of the reasons that known systems do not work as long as would be desirable.² Therefore new viologen derivatives should be synthesized which are more stable against hydrogenation.

To achieve a cyclic water-splitting process a second catalyst (e.g. RuO₂³ or IrO₂⁴) for water oxidation [reaction (3)] is necessary.



In their monoreduced form viologen radicals have an unpaired electron. These blue radicals are very sensitive to oxygen⁵ [reaction (4)].



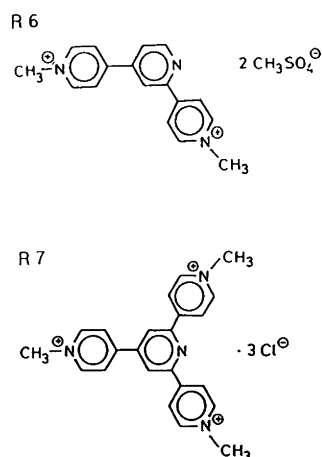
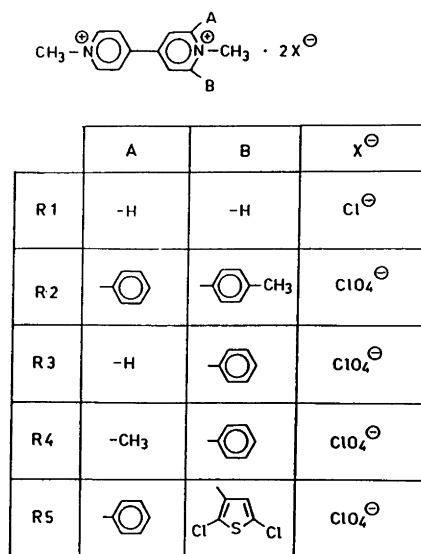
Since a practical water-splitting system is never free of oxygen, the electron relay radicals should be as stable as possible with respect to oxygen. In combined systems (H₂ and O₂ production) this is essential. In the search for new electron relay compounds, it is therefore also important that their radicals show significant kinetic differences in their reaction with O₂ and H₂-producing catalysts, favouring the heterogeneous catalyst. Furthermore, oxygen-stable radicals (reduced forms of molecules) which show a colour other than their oxidized form, could be of interest for other applications (e.g. smart windows or display colours).

We have investigated new 2,6-disubstituted derivatives of methyl viologen and two related compounds and their radicals in systems with Ru(bipy)₃²⁺ and some colloidal platinum catalysts and compared them with methyl viologen.

Experimental

Materials. Tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate (**R1**) was from Janssen Chemica and methyl viologen hydrate (**R1**) was from Aldrich. The syntheses of the relay compounds 1,1'-dimethyl-2-phenyl-6-(*p*-tolyl)-4,4'-bipyridinium diperchlorate (**R2**), 1,1'-dimethyl-2-phenyl-4,4'-bipyridinium diperchlorate (**R3**), 6-phenyl-1,1',2-trimethyl-4,4'-bipyridinium diperchlorate (**R4**), 1,1'-dimethyl-2-phenyl-6-(2,5-dichloro-3-thienyl)-4,4'-bipyridinium diperchlorate (**R5**), and 1,1''-dimethyl[4,2';4',4''']terpyridinium methylsulfate (**R6**) have been described elsewhere.⁶ 1,1'',1'''-trimethyl[4,2';4',4'';6',4''']quaterpyrid-

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inium trichloride (**R7**) was prepared according to Ref. 7. EDTA was Titriplex III from Merck. $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ was prepared as described in Ref. 8; twice-distilled water was used in all experiments.

The catalysts used were as follows. **PtC1** was a colloidal Pt catalyst with 5 g Carbowax-20M per g Pt for stabilization prepared by a procedure described elsewhere.⁹ The concentration of Pt was 142 mg l^{-1} ; the particle size was about 3 nm (TEM). **PtC1** was the same as **PtC2** except for the polymer concentration, in this case 10 g per g Pt. **PtT1** was a platinum-TiO₂ catalyst, produced by supersonic agitation of colloidal platinum with colloidal TiO₂ and 2% PVA solution;¹⁰ ready for use, the catalyst contained the following concentrations: 119 mg Pt l^{-1} , $504 \text{ mg TiO}_2 \text{ l}^{-1}$ and 0.1% PVA. **PtT2** was the same as **PtT1** except for the TiO₂ concentration, in this case 838 mg l^{-1} . **PtT3** was prepared by photoplatinization of a mixture of 0.1 ml 10% $H_2PtCl_6 \cdot 6H_2O$, 2.64 ml colloidal TiO₂ ($10.7 \text{ g TiO}_2 \text{ l}^{-1}$)¹⁰ and 22.57 ml H₂O; 70 min irradiation with a 450 W xenon lamp was followed by stabilization with 2% PVA solution. Concentrations of the ready-for-use catalyst were as follows: 142 mg Pt l^{-1} , $884 \text{ mg TiO}_2 \text{ l}^{-1}$ and 0.1% PVA; pH 1.8.

The reaction mixtures had the following concentrations: $4.82 \times 10^{-4} \text{ M Ru(bipy)}_3^{2+}$, $1.93 \times 10^{-3} \text{ M relay}$, $9.59 \text{ mg Pt l}^{-1}$, $4.18 \times 10^{-2} \text{ M EDTA}$, $9.65 \times 10^{-2} \text{ M NaAc}$ with HAC buffer (1:1); there were two exceptions: the concentrations of EDTA in the systems with **R2** and **R5** were 3.22×10^{-2} and $2.57 \times 10^{-2} \text{ M}$, respectively. The pH was 4.8 in all experiments. 3.11 ml of each mixture were purged well with pure nitrogen and then the charging and discharging experiments were carried out. Subsequently the mixtures for the discharging experiments were used for the hydrogen-producing experiments.

Charging and discharging of the radicals. The equipment for these experiments was an Oriel 450 W xenon lamp with

a water filter, condenser optics and a 400 nm cut-off filter as an actinic light source. A fast shutter with a closing time of 1 ms was installed in front of the cell holder. A 30 W tungsten lamp, with one monochromator (Zeiss M4 QII) in front of and one (Oriel) behind the cell holder, both with a 0.5 mm slit position, was used as the analytic light (Fig. 1). A 100 mm² silicon cell (RCA N-type PIN photodetector, C30810) measured the absorptions of the relay radicals present during the charging and discharging phases.¹¹

After a few seconds of irradiation (the solution was stirred during the charging period), a steady state was reached and the shutter was closed. The blue radicals transferred their electrons (received during the charging process) in <1 s to the catalyst.

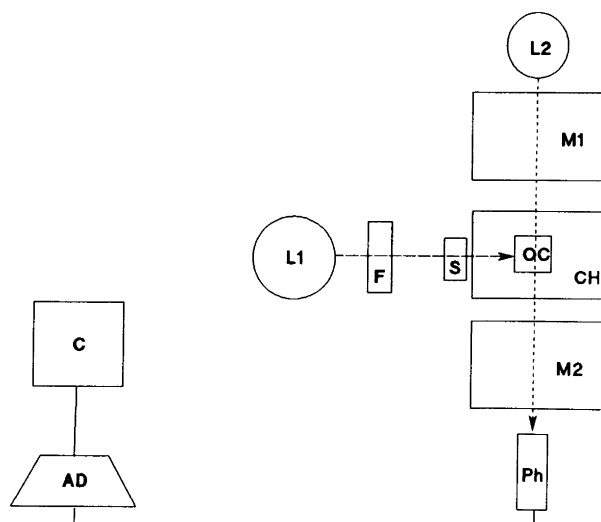


Fig. 1. Equipment for charging and discharging experiments: L1, 450 W xenon lamp; L2, 30 W tungsten lamp; F, 400 nm cut-off filter; M1, Zeiss monochromator; M2, Oriel monochromator; S, shutter; CH, cell holder; OC, optical cell; Ph, photodetector; AD, analogue-digital converter; C, computer.

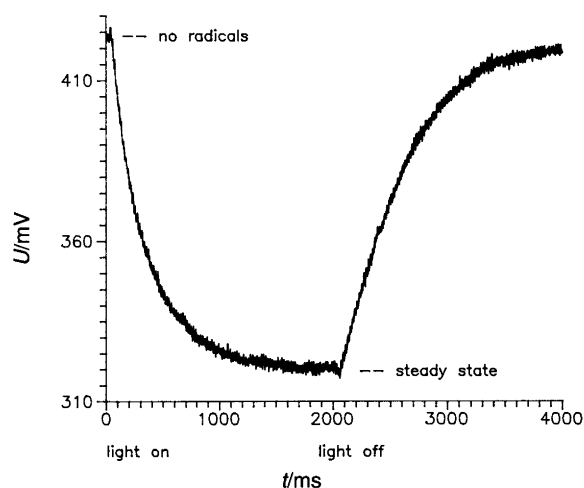


Fig. 2. Typical charging and discharging curves for the system **R3/PtT2**; for conditions see the Experimental section.

The measured voltages were digitized with a scanning rate of 1 point per ms and computed. The discharging data followed a first-order reaction law for compounds **R1–R6**. The order of the discharging reaction with **R7** was between 1 and 2. A typical charging and discharging curve is shown in Fig. 2.

Hydrogen production measurements. A slide projector with a 150 W halogen filament lamp, a water filter, a K-45 filter for the first 2 h irradiation and a 400 nm cut-off filter (instead of the K-45) for a further 2 h were used. The reaction mixture was in a 1 cm optical cell with a total volume of 5.60 ml, which was fitted with a septum. During irradiation the solutions were stirred and every 30 min a sample of the gas in the room housing was analyzed with a GC-6000 gas chromatograph (Carlo Erba Instruments) fitted with HWD-430 and 2 m packed columns (5A molecular sieve).

The loss of hydrogen caused by sampling was corrected. The hydrogen production rate, r_{H} , and quantum yield, Φ , were calculated using the data obtained in the first 2 h. For ferrioxalate actinometry a 0.15 M $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ solution was used to determine the number of photons.⁸ Φ is

Table 1. Absorption coefficients (ϵ) of the electron relay radicals (in $\text{M}^{-1} \text{cm}^{-1}$).

R1:	$\epsilon(603 \text{ nm}) = 12000^a$	
R2:	$\epsilon(590 \text{ nm}) = 8620;$	$\epsilon(380 \text{ nm}) = 12600$
R3:	$\epsilon(610 \text{ nm}) = 11500;$	$\epsilon(392 \text{ nm}) = 19200$
R4:	$\epsilon(605 \text{ nm}) = 8400;$	$\epsilon(393 \text{ nm}) = 16000$
R5:	$\epsilon(575 \text{ nm}) = 8200;$	$\epsilon(373 \text{ nm}) = 12500$
R6:	$\epsilon(650 \text{ nm}) = 9300;$	
R7:	$\epsilon(633 \text{ nm}) = 113000^b$	

^aFrom Ref. 6. ^bFrom Ref. 12.

given by eqn. (5), where $I = 4.85 \times 10^{16} \text{ photon s}^{-1} \text{ cm}^{-2}$ (between 400 and 500 nm) and n_{H_2} is the number of molecules of H_2 in the gas phase and in solution per s. The absorption coefficients were measured with a Hitachi 220 spectrophotometer. The results are presented in Table 1.

$$\Phi = 2n_{\text{H}_2}/I \quad (5)$$

Results and discussion

Charging and discharging of the radicals. Measurements of the discharging rate constants are complicated by the fact that heterogeneous catalysts have an activation period, and that small traces of oxygen may falsify the results. (Fig. 3 shows the computation of a discharging experiment, following first-order kinetics, while rate constants are given in Table 2.) Therefore about five blind experiments were run at the beginning of the experiments, followed by four to nine measurements. The radical of **R5** was reversibly adsorbed on the catalyst and formed a blue precipitate which slowly dissolved after the light was turned off. During irradiation these reaction mixtures turned dark blue.

Former studies showed that the reduced form of **R7** forms different radicals, and when it is totally reduced in a photoelectrochemical cell at a potential of -0.66 V (glassy carbon), a transient peak at 577 nm (solution steel blue) disappears. Only the main absorption peak in the visible range remains at 633 nm (giving a turquoise solution) with a very high absorption coefficient ($\epsilon = 113 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).¹² Coulometric analysis proved that up to six electrons per molecule of **R7** were transferred, depending on the pH.¹² Redox reactions take place between the different radicals of **R7**. This could be an explanation for the different discharging behaviour (reaction law between first and second order). The formation of stable triradical dimers could be the reason for the slower discharging reaction.

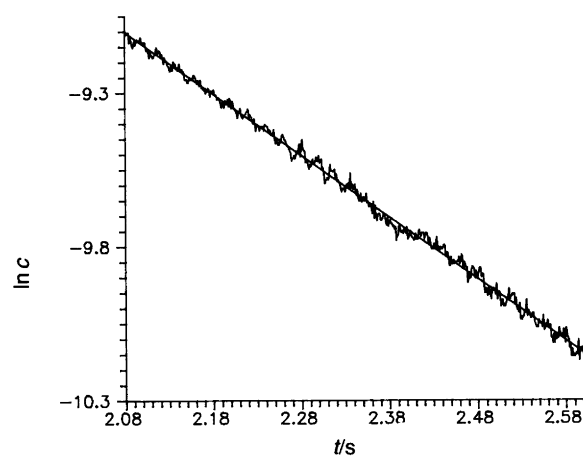


Fig. 3. Computation of a discharging experiment, following a first-order reaction law (data from Fig. 2).

Table 2. Discharging reaction rate constants (in s^{-1}), following a first-order reaction law (for conditions see Experimental section).

Relay	PtC1	PtC2	PtT1	PtT2	PtT3
R1	6.7	5.1	0.62	0.65	3.0
R2	4.9	4.8	—	—	2.5
R3	3.5	3.0	—	—	2.2
R4	14.0	12.0	7.0	7.5	7.9
R5	0.006	—	—	—	—
R6	0.5	0.8	0.44	0.5	0.07
R7^a	2.1 (5.8)	1.7 (4.7)	0.9 (1.0)	1.1 (1.4)	0.72 (0.9)

^aThe values in parenthesis for **R7** were calculated according a second-order reaction law (in $10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$).

These stable radicals show unusually high stability towards oxidation with oxygen. Unlike any other known relay molecule for H_2 production almost no change in colour was seen when an aqueous solution of **R7** radicals was poured from one glass into another.⁶

These results encouraged us to compare the discharging behaviour of the radicals of **R7** with those of **R1** under various conditions.

(a) The discharging behaviour of the radicals with a catalyst under an air atmosphere showed a considerable increase in the reaction rate constant k_1 with **R1** compared with k_1 under nitrogen. The reason for this is the addition of the rates of reactions (2) and (4). This effect was not observed with **R7**.

(b) The discharging behaviour of the radicals under an air atmosphere without a catalyst showed a decrease in k_1 for **R1** with the number of experiments. In the first experiment k_1 was about five times higher than in the following experiment, a result which corresponded to a very fast consumption of dioxygen molecules by the radicals of **R1** in the solution. After the solution was shaken k_1 returned to its initial value. Our measurements with radicals of **R1** gave

Table 3. Hydrogen production rate, r_H (in $10^3 \text{ ml H}_2/\text{ml solution min}$), during 2 h irradiation with a K-45 filter and a 150 W lamp; Φ = quantum yield (in %).

Relay	PtC1		PtC2		PtT1		PtT2		PtT3	
	r_H	Φ	r_H	Φ	r_H	Φ	r_H	Φ	r_H	Φ
R1	4.9	25	4.7	24	3.7	19	4.2	21	3.6	19
R2	3.5	18	3.0	17	—	—	—	—	2.8	14
R3	3.6	19	3.4	18	2.2	11	3.6	19	3.1	18
R4	5.0	26	3.8	20	3.5	19	3.9	21	3.8	20
R5	0.2	1	—	—	—	—	—	—	—	—
R6	0.3	2	0.8	4	0.9	5	1.1	6	0.9	5
R7	2.2	11	2.1	11	1.9	10	2.2	11	1.4	7

the result that reaction (4) was catalysed by platinum (more than one order of magnitude faster). In contrast to **R1**, the influence of O_2 on the radicals of **R7** was negligible.

(c) The discharging behaviour of the radicals under a nitrogen atmosphere without a catalyst showed that the reduced form of **R1** did not practically unload. The behaviour of **R7** radicals was the same as under an air atmosphere.

Hydrogen production measurements. The Φ -values were calculated from the total amount of hydrogen (gas phase and solution) (Fig. 4 and Table 3). To compare the efficiencies of the different systems, one should make a comparison between the quantum yields, because the data for r_H depend on the power of the actinic light source. At the beginning of the experiments the solutions are free of hydrogen, and the first hydrogen produced will be used to saturate the solution and the catalyst. The concentration and the nature of the protective colloid is of great importance.¹³ Concentrations that were too low led to precipitation of the catalyst, and concentrations too high reduced the efficiency of electron transfer between the electron relay and the catalyst.

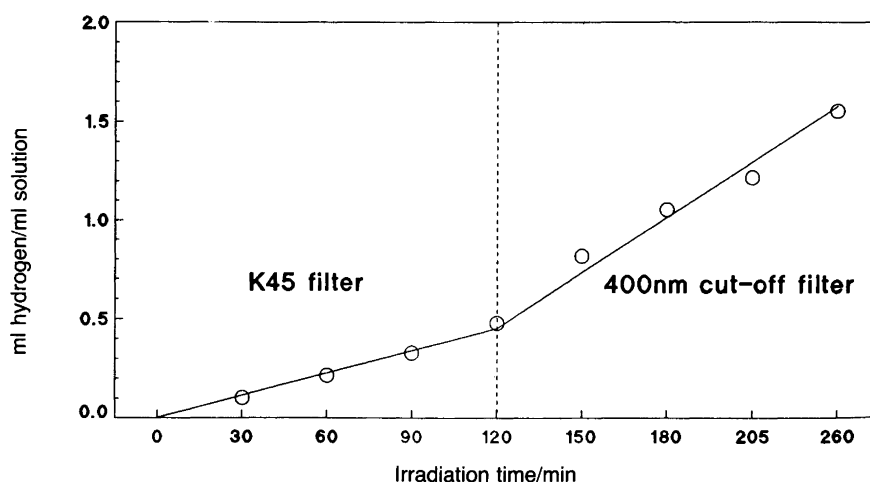


Fig. 4. Typical hydrogen production curve for the system **R4/PtT2**; for conditions see the Experimental section.

The different stabilities of **R1** and **R7** radicals against oxygen were investigated using the following procedure. A 3 ml solution (10^{-3} M relay, 1.67×10^{-4} M Ru(bipy) $_3^{2+}$ and 6.67×10^{-2} M EDTA) was purged well with nitrogen. The solution was irradiated with a 150 W halogen filament lamp until a steady state was reached (ca. 30 min). Subsequently the mixture in the cell was exposed to air and stirred. The decay of the radical absorption was measured with a photometer. It was found that the **R7** radicals were about one order of magnitude more stable against oxygen than the **R1** radicals ($k_1 = 2 \times 10^{-3}$ s $^{-1}$ for **R1** and $k_1 = 2 \times 10^{-4}$ s $^{-1}$ for **R7**). The diffusion of oxygen influenced the discharging rate using this measuring technique.

For a further investigation of the affinity of the radicals **R1** and **R7** towards O $_2$, hydrogen production measurements were made with solutions (with Pt) under an air atmosphere. **R7** produced hydrogen unaffected by oxygen. The radicals of **R1**, although they produced hydrogen, reacted very rapidly with dissolved oxygen. We suggest that at first the radicals of **R1** react according to reaction (4) with all dissolved oxygen and then according to reaction (2). The fact that **R1** produced hydrogen although air was present in the gas phase is explained with the slow [relative to reaction (4)] diffusion of oxygen in aqueous solution.

Conclusions

We have found that one of the investigated radicals, **R7**, combined extremely high stability against oxygen with sufficiently high discharging rates and H $_2$ production. After 1 h of a hydrogen production experiment **R1** had consumed almost all oxygen present in the cell (4 mol O $_2$ per mol **R1**). Under the same conditions with **R7** practically no oxygen was consumed. The reasons for this unusual kinetic

differentiation are still unclear. Further work on this promising relay compound and its derivatives is in progress.

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