Light-induced Electron Transfer from Tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ to a Nickeldithiolene in Homogeneous and Heterogeneous Systems

Rudolf Frank and Hermann Rau

FG Physikalische Chemie, Institut für Chemie, Universität Hohenheim, Stuttgart

Z. Naturforsch. **37a**, 1253–1258 (1982); received September 1, 1982

We have investigated the reduction of Nickel-tetraphenyldithiolene by 2-aminonaphthalene with Ru(bipy)$_3^{2+}$ as a photocatalyst and found a quantum yield of approximately 1% for the conditions of our homogeneous system. The lifetime of Ru(bipy)$_3^{2+}$ is increased from 600 to 800 ns when micelle formation in aqueous solutions of anionic surfactants takes place. No such change in lifetime is found in nonionic micelles. In a three compartment system the light driven electron transport from one aqueous compartment containing the Ru(bipy)$_3^{2+}$/EDTA system through a membrane containing Ni-dithiolene in an organic solvent to the second aqueous compartment containing Na$_3$[Fe(CN)$_6$] is investigated. It is shown that direct electron transfer from the excited ruthenium complex to Ni-dithiolene across the phase boundary can be effected by the action of an anionic surfactant.

1. Introduction

Dithiolene complexes may play a role in suitably designed systems for photochemical hydrogen production from water. Kisch et al. [1] have used these complexes as photocatalysts in hydrogen production in THF/water solution. Little is known about the mechanism of that process except that UV-irradiation is required, the dithiolenes themselves do not catalyze the process, and that THF is oxidized. We investigated the Ru(bipy)$_3^{2+}$ sensitized reduction of the nickel-tetraphenyldithiolene complex (NiTPDT) in homogeneous solution. This reaction, unfortunately, does not lead to liberation of hydrogen gas from water.

[NiTPDT] has been used by Grimaldi and Lehn [2] as a carrier for electrons through an artifical membrane separating two compartments containing aqueous solutions of $K_2S_2O_4$ and $K_3[Fe(CN)_6]$, respectively. A heterogeneous system of this kind may become important in a light induced charge separation process if the light can induce at the same time charge separation and electron transfer across the phase boundary. We investigated such a light driven electron transport by [NiTPDT] through an artifical membrane.

2. Results and Discussion

Electron transfer from Ru(bipy)$_3^{2+}$ to [NiTPDT]^0 may be observed in two ways: we may observe the donor's emission in stationary or dynamic quenching experiments or we may observe the acceptor's transient or permanent reduction products. We have used approaches in homogeneous and heterogeneous systems.

2.1. *The Quenching Experiments in Homogeneous Solution*

Stationary fluorescence measurements of the Ru(bipy)$_3^{2+}$-ion in the presence of increasing amounts of [NiTPDT]^0 in THF/water (10 : 1) can be analyzed in terms of Stern-Volmer kinetics (Figure 1). As the sensitizer as well as the quencher absorb at the excitation wavelength of 450 nm and at the wavelength of 600 nm used for analyzing the emission the experimental fluorescence intensities were corrected by [3]

$$k = k_A \cdot k_E = \frac{2.303\,E_{450}}{1-10^{-E_{450}}} \cdot \frac{2.303\,E_{600} \cdot 10^{E_{600}}}{10^{E_{600}}-1},$$

where E is the absorbance. With $\tau_0(\text{Ru(bipy)}_3^{2+}) =$ 800 ns a bimolecular quenching constant of $k_q = 8.5 \pm 0.6 \cdot 10^9\,\text{l mole}^{-1}\,\text{s}^{-1}$ is determined from the Stern-Volmer plot which indicates diffusion control of quenching.

The dynamic fluorescence quenching at low quencher concentrations can be presented by a linear Stern-Volmer plot, too. At higher quencher concentrations the τ_0/τ-ratio does no longer follow the Stern-Volmer linear relation but approaches a limiting value of about 400 ns. This divergence of stationary and dynamic Stern-Volmer plots has been

---

Reprint requests to Prof. Dr. H. Rau, Institut für Chemie, Garbenstr. 30, D-7000 Stuttgart 70 (Hohenheim).

0340-4811 / 82 / 1100-1253 $ 01.30/0. — Please order a reprint rather than making your own copy.

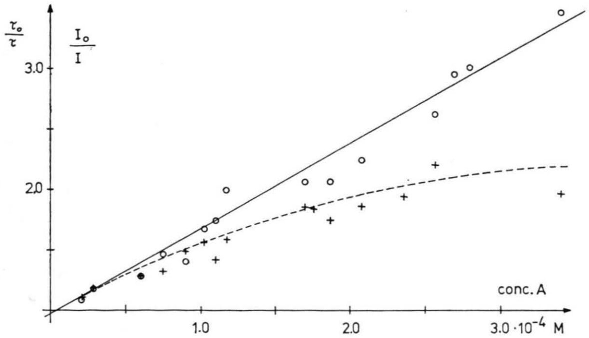


Fig. 1. Stationary (○) and dynamic (+) Stern-Volmer plot of the quenching of $Ru(bipy)_3^{2+}$ by $[NiTPDT]^0$.

taken as an indication of an exciplex mechanism of energy or electron transfer [4].

$Ru(bipy)_3^{2+}$-emission is also quenched by the anion $[NiTPDT]^-$. In THF/water the quenching reaction cannot be evaluated as $[NiTPDT]^-$ in this solvent is very sensitive to oxygen which never could be excluded totally during the preparation of the samples. In acetonitrile the O_2 influence is much less and a stationary Stern-Volmer evaluation leads to a quenching constant of $k_q = 4.7 \cdot 10^{10}\,l\,mole^{-1}\,s^{-1}$ which is slightly higher than the literature value of k_{diff} ($2 \cdot 10^{10}\,l\,mole^{-1}\,s^{-1}$ [5]).

2.2. *Sensitized Photoreduction of $[NiTPDT]^0$ in Homogeneous Solution*

We observed a permanent photoreduction of $[NiTPDT]^0$ by 2-aminonaphthalene (AN) as an electron source in homogeneous THF/H_2O (10 : 1) solution when $Ru(bipy)_3Cl_2$ was used as a photosensitizer. Several other amines were tested as reductants in this experiment, some of them e. g. diphenylamine or triethanolamine, are able to reduce $[NiTPDT]^0$ without light and $Ru(bipy)_3^{2+}$.

In order to characterize the system we made some tests: (a) if a solution of $[NiTPDT]^0$ in THF/water is irradiated by visible light the complex proves to be stable. There is no photocatalytic activity leading to hydrogen evolution in accordance with Kisch's experiments [1]. (b) If $Ru(bipy)_3Cl_2$ is added only a small decrease of the $[NiTPDT]^0$ absorption is observed. (c) If AN is then added a fast photoreaction occurs (Figure 2 a). (d) Irradiation of $[NiTPDT]^0$ and AN without $Ru(bipy)_3^{2+}$ does not change the absorption noticeably.

The reaction products are $[NiTPDT]^-$ and oxidation products of AN. Two isosbestic points are observed at 543 and 455 nm. These isosbestic points are blurred at prolonged irradiation most probably by two events: $[NiTPDT]^-$ is further reduced to $[NiTPDT]^{2-}$ and the oxidation products of AN may absorb in the visible region.

From the existence of isosbestic points and the information from Mauser diagrams [6] we conclude that the photoreaction is a spectroscopically uniform reaction at least in the early phases and so we evaluate the reaction spectra up to about 10% extent of reaction. Kisch has presented the absorption spectrum of the UV-irradiated nickeldithiolene complex which is assumed to be active in his hydrogen evolution system [7]. Certainly this photocatalyst is not identical with either $[NiTPDT]^-$ or $[NiTPDT]^{2-}$ as the absorption spectra differ and as we were not able to produce hydrogen.

2.2.1. Kinetic Analysis of the Sensitized Photoreduction of $[NiTPDT]^0$ in Homogeneous Solution

In the sensitized photoreduction of $[NiTPDT]^0$ two mechanisms may be active: (a) The sensitizer may be quenched and oxidized by $[NiTPDT]^0$ and subsequently re-reduced by the amine or (b) the sensitizer may be quenched and reduced by the amine and subsequently reoxidized by $[NiTPDT]^0$. Moreover both mechanisms may be active simultaneously.

We have no indication of the participation of the solvent (as is the case upon UV-irradiation [1]) so only reactions between the sensitizer S, $Ru(bipy)_3^{2+}$, the acceptor A, $[NiTPDT]^0$, and the reductant R, AN, are to be considered. We have to keep in mind that R is in high excess over S and that stable reaction products of R require the transfer of two electrons [8]. We have tried to do a kinetic analysis on this basis by evaluating the time development of the absorbance at 600 nm (Figure 3). A nice fit by $y = a + b\,e^{cx}$ ($E = 0.365 + 0.078 \exp[-3.635 \cdot 10^{-4}\,t]$) is possible and this type of equation is in agreement with the straightforeward oxidative or oxidative plus reductive mechanisms. But the numerical evaluation would require $E_\infty = \varepsilon_{A^-} \cdot c_0 = 0.126$ instead of 0.365 and negative rate constants, which is impossible. We have, however, to consider the participation of $[NiTPDT]^-$ in quenching or, perhaps, some back reaction. The former is indicated by the virtual constancy of τ of $Ru(bipy)_3^{2+}$ [9] at concentrations $> 2 \cdot 10^{-4}$ M and would attribute the large deviation

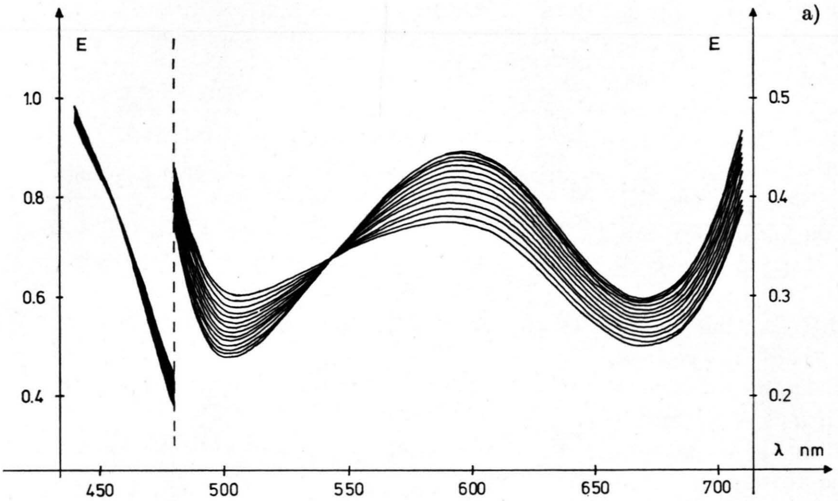
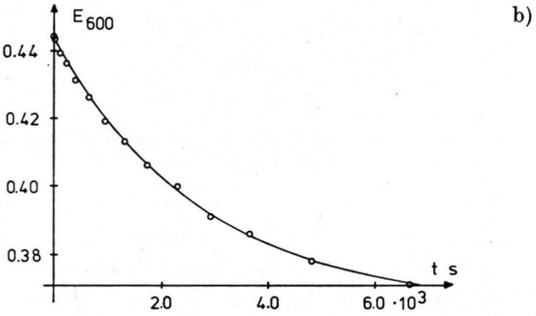


Fig. 2. Photoreaction of $[NiTPDT]^0$ ($2.3 \cdot 10^{-4}$ M) in the presence of $Ru(bipy)_3Cl_2$ ($2 \cdot 10^{-5}$ M) and 2-aminonaphthalene (10^{-2} M) in THF/H_2O 10:1. Excitation wavelength 436 nm. (a) reaction spectra (b) change of absorbance with irradiation time.



of E_∞ from the expected value of 0.126 to inaccuracy of the fitting procedure which comprises but 10% of the reaction. The latter would lead to a quasi photostationary state at only 25% reduction of $[NiTPDT]^0$. We prefer the first alternative.

We can still use the curve fitting procedure to obtain an initial slope in order to get an idea about the virtual differential quantum yield [11] of the photoreduction of $[NiTPDT]^0$ given by

$$\Phi_A(0) = \frac{dc_{A0}/dt}{I_{abs}(0)} = \frac{dE_{600}(0)/dt}{\Delta\varepsilon_{600} I_{abs}(0)} .$$

From the experiment in Fig. 2 and Fig. 3 we obtain $dE_{600}(0)/dt = -2.835 \cdot 10^{-5}\,s^{-1}$. With $\varepsilon_{A,600} = 1890\,l\,mole^{-1}\,cm^{-1}$, $\varepsilon_{A^-,600} = 540\,l\,mole^{-1}\,cm^{-1}$, with the 436 nm intensity of $I_0 = 9.87 \cdot 10^{-9}$ Einstein $s^{-1}\,cm^{-2}$, $E_{436}(0) = 0.86$, $c_D = 2.05 \cdot 10^{-5}$ M and $\varepsilon_{D,436} = 12600\,l\,mole^{-1}\,cm^{-1}$ we find

$$\Phi_A(0) = 0.82\% .$$

This is the maximum yield of $[NiTPDT]^0$ reduction and the yield drops to zero when the quasi stationary state is reached.

2.3. The Lifetime of $Ru(bipy)_3^{2+}$ Emission in Heterogeneous Systems

Rather diverging values of the lifetime of excited $Ru(bipy)_3^{2+}$ complexes in micellar solutions are reported in the literature [12 – 16] ranging from 480 to 800 ns. So we re-investigated the complex's lifetime in micelle-forming Na-dodecylsulphate (SDS), Na-dodecanate (SDC), Na-perfluorooctanesulphonate, Na-perfluorooctanate and Triton-X-100 as function of the tenside concentration. We chose small concentrations of $Ru(bipy)_3Cl_2$ in order to avoid aggregation below the critical micelle concentration (CMC) as observed by Rogers [12, 15] and to avoid double occupation of micelles above the CMC.

Some results are shown in Figure 3. We observe monoexponential decays of the complex's emission below ($\tau = 590 \pm 40$ ns) as well as above the CMC ($\tau = 800 \pm 40$ ns) in anionic surfactants. In Triton-X-100 a non-ionic surfactant, $\tau = 530 \pm 30$ ns below

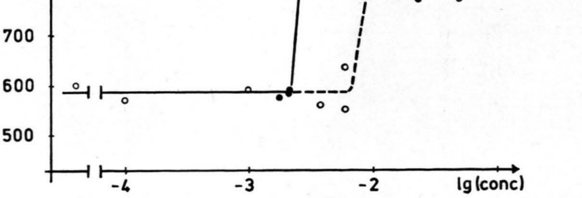


Fig. 3. Lifetime of $Ru(bipy)_3^{2+}$ as a function of tenside concentration. ○ lifetime in H_2O/SDS. ● lifetime in dimethylamonium-perfluoroctansulfonat.

and above the CMC. The emission spectrum of the $Ru(bipy)_3{}^{2+}$-ion is red-shifted by 20 to 25 nm in Na-dodecylsulphate and Na-dodecanate micelle solution, relative to that in water. The emission spectrum is unchanged, however, in micellar solutions of the perfluoro-tensides and Triton-X-100.

The lifetime of the $Ru(bipy)_3{}^{2+}$-complex can, accordingly, be used to determine the CMC of anionic surfactants [17]. We conclude from these experiments that in anionic surfactants the $Ru(bipy)_3{}^{2+}$-ion is part of the Stern-layer [14], but that no attraction exists to the nonionic micelles. The shift of the emission spectrum may indicate an interaction of the hydrocarbon chains and ligands of the ruthenium complex: a similar spectral change is observed in homogeneous solution of the Ru-complex with three bipyridine ligands carrying two long hydrocarbon chains each [18]. The micellar structure seems to be loose and to permit access for the complex to the hydrocarbon core part. This interaction is absent in the perfluoro-micelles and Triton-X-100.

2.4. *The Sensitized Photoreaction of [NiTPDT]⁰ in a Heterogeneous System*

For these experiments we have used a three compartment heterogeneous system very similar to that of Lehn's [2]. Two aqueous phases are separated by an organic phase (diphenylether) supported by a millipore filter (Figure 4).

Lehn has shown that electrons from aqueous $S_2O_4{}^{2-}$ are transported by $[NiTPDT]^-$ to the aqueous $[Fe(CN)_6]^{3-}$ compartment and that the cotransport of a K^+-ion may be effected by a crown ether. We have used the light energy as the driving force instead of chemical energy.

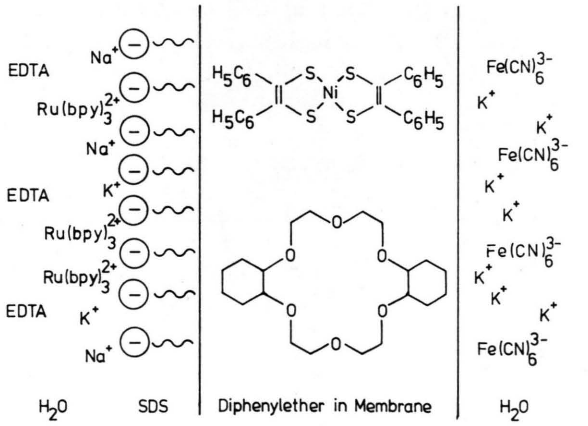


Fig. 4. Schematic diagram of the electron transport through membranes. Components of reaction system VI.

Table 1. Experimental parameters and transport rates in heterogeneous nickel dithiolene mediated electron transfer (see Figure 4).

System No.	Contents of compartment 1	Rate of reduction of $Fe(CN)_6{}^{3-}$	
		irradiation	μmole h⁻¹
I	—	±	0
II	$5 \cdot 10^{-2}$ M $Na_2S_2O_4$ (no light) KCl 10^{-1}	—	0.2
III	$2 \cdot 10^{-5}$ Ru(bipy)$_3$Cl$_2$ 10^{-1} KCl	+	0
IV	$2 \cdot 10^{-5}$ Ru(bipy)$_3$Cl$_2$ $1 \cdot 10^{-3}$ MV^{2+}/KCl	+	0
V	$2 \cdot 10^{-5}$ M Ru(bipy)$_3$Cl$_2$ $1 \cdot 10^{-3}$ M MV^{2+} $1 \cdot 5 \cdot 10^{-2}$ M EDTA/KCl	+	0.2
VI	$2 \cdot 10^{-5}$ M Ru(bipy)$_3$Cl$_2$ $1 \cdot 5 \cdot 10^{-2}$ M EDTA SDS 10^{-2}/KCl	+	0.1

Typically compartment 2 contained $8 \cdot 10^{-3}$ M $[NiTPDT]^0$ and 10^{-1} M dicyclohexano-18-crown-6 in diphenylether and compartment 3 contained $6 \cdot 10^{-4}$ M $Na_3Fe(CN)_6$ in water. The 420 nm band of the $Fe(Cn)_6{}^{3-}$-ion was monitored as an indicator of electron transport through the system. Compartment 1 contained a 10^{-1} M KCl solution in water and the materials listed in Table 1 for six different experiments. The redox potentials of the compounds relevant for electron transport are (a) in compartment 1: $Ru(bipy)_3{}^{3+/2+}$: $E_0 = +1.26$ V, $Ru(bipy)_3{}^{3+/2+*}$ -0.86 V, (b) in compartment 2: $[NiTPDT]^{0/1-}$ 0.388 V (halfwave potential converted to Standard Hydrogen), (c) in compartment 3: $[Fe(CN)_6]^{3-/4-}$ 0.360 V. From thermodynamic reasons the electron flow from excited $Ru(bipy)_3{}^{2+}$ to $Fe(CN)^{3-}$ is downhill.

Also in Table 1 the rates of $Fe(CN)_6{}^{3-}$ reduction are listed. In system II we reproduced Lehn's $Na_2S_2O_4$ experiments for comparison. Under our conditions the $[NiTPDT]^0$ was reduced nearly totally to the anion. This may be seen from the change in colour of the organic phase. The transfer of the electron from the $[NiTPDT]^-$-ion to the $Fe(CN)_6{}^{3-}$-ion across the phase boundary 2/3 seems to be the rate limiting step, and we assume maximum efficiency of electron transport.

The experiment in system III shows that the direct transfer of an electron from the excited Ru(bipy)$_3^{2+}$ to [NiTPDT]^0 across the phase boundary is not possible. This might be due to the relatively short lifetime of the excited ruthenium complex. In order to create a longer lived intermediate we used in systems IV and V methylviologen (MV Cl_2) as an electron relay [19]. In system V, with EDTA as a reductant, this was quite efficient, the blue colour of the MV$^+$-radical ion developed in compartment 1 and a change in colour in compartment 2 was observed. The electron transport through the membrane was as fast as with $Na_2S_2O_4$ as a reductant. But although light is involved in creating the reductant in compartment 1 it is not the light that causes the trans-boundary transport of the electron.

A direct light induced transfer of the electron from Ru(bipy)$_3^{2+}$ to [NiTPDT]^0 across the phase boundary can be effected if an anionic tenside (we used SDS) is added to the Ru(bipy)$_3$Cl$_2$/EDTA solution in compartment 1 (system VI). From the experiments on SDS-micelles we known that the Ru(bipy)$_3^{2+}$ is preferentially dissolved in the Stern-layer. We believe that SDS forms an interphase layer between water and diphenylether and accumulates the ruthenium-complex there.

3. Conclusion

The photoreduction of [NiTPDT]^0 by excited Ru(bipy)$_3^{2+}$-complexes is only permanent if the electron transferred is replenished by a second electron transfer from a reductant as e. g. an amine, as is well known e. g. from the work of Grätzel et al. [20], who have also studied the photoreduction of Ru(bipy)$_3^{2+}$. This requires contact between [NiTPDT]^0 and the excited ruthenium complex. In our heterogeneous system the electron is driven directly across the phase boundary by light if the ruthenium complex is accumulated in the phase boundary, e. g. by modification of the boundary by an anionic surfactant. The macroscopic membrane hosts the dithiolene electron acceptor. Experiments with reversible dithiolene donors are under way as the electron flow from a reversible electron donor to the ruthenium complex is more interesting than the process described in this paper. We aim at the substitution of the irreversible oxidation of the amine by the reversible oxidation of a dithiolene. Ultimately we hope to compensate its electron loss by coupling the dithiolene redox-system to the O_2/OH^--part of the water cleaving system.

4. Experimental Part

[NiTPDT]^0 was prepared according to Schrauzer et al. [21] and chromatographed at silica columns. AN was purified by sublimation. SDS (MERCK) was extracted by n-hexane in a Soxleth apparatus for 4 days to remove dodecanol [22]. All other chemicals were of analytical grade.

Absorption spectra were taken by a ZEISS DMR 10 spectrophotometer, emission spectra by a Farrand MK 1 spectrofluorometer. Lifetime measurements were made by excitation with a LAMBDA-Physics Multigas Laser EMG 500 working with N_2 as an active medium. The emission wavelength was selected by an ORIEL double monochromator GM 7240, the decay curve measured by a RCA 31034 A photomultiplier in a Knott base with kathode follower amplifier and displayed on a Tektronix storage oscilloscope 7834.

Photoreactions in homogeneous solutions were induced by a Philips HPK 125 mercury lamp with 436 nm UV-PIL filter by Schott. For illumination of the heterogenous systems the light source of a slide projector was used.

Standard one centimeter sample cells were used for the reactions in homogeneous solutions which were stirred. The cells for heterogeneous systems were assembled from two polystyrene 1 cm square cells. One window was removed from each of the cells and a Sartorius membrane filter sheet (polyamide, 0.05 µm pores) was placed between the two cells by clamping them together. The filter was soaked with NiTPDT and the crown ether dissolved in diphenyl ether [2]. The clamped unit was constructed so as to fit to the sample compartment of the ZEISS spectrophotometer.

Lifetimes and the photochemical quantum yields were calculated by means of a 4452 Tektronix computer. The algorithm of Marquardt [23] was used for the nonlinear regressions.

Acknowledgement

This work has been partly supported by the Fonds der Chemischen Industrie Frankfurt (Main).

[1] R. Henning, W. Schlamann, and H. Kisch, Angew. Chem. **92**, 664 [1980] and Lit. cited there; R. Battaglia, R. Henning, and H. Kisch, Z. Naturforsch. **36 b**, 396 (1981).

[2] J. J. Grimaldi and J. M. Lehn, J. Amer. Chem. Soc. **101**, 1333 [1979].

[3] R. Frank and H. Rau, J. Photochem. **18**, 281 [1982].

[4] T. S. Fang, R. E. Brown, C. L. Kwan, and L. A. Singer, J. phys. Chem. **82**, 2489 [1978].

[5] N. Turro, Modern Molecular Photochemistry, Benjamin Cummings, Menlo Park 1978, p. 314.

[6] (a) H. Mauser, Formale Kinetik, Düsseldorf 1954; Z. Naturforsch. **23 b**, 1025 [1968]; (b) H. Mauser, Formale Kinetik, p. 134.

[7] H. Kisch, private communication.

[8] e.g. E. Ford, J. W. Ötvös, and M. Calvin, Nature London **274**, 507 (1978).

[9] If τ is constant because the product quenches as well as the educt we expect a decay exponential in irradiation time for a sensitized reaction. Otherwise a time axis transformation $p' = 1/\tau_0 \int \tau(t)\,dt$ is necessary for exponentiality [10]. t is the irradiation time.

[10] R. Blume, O. Schuster, and H. Rau, J. Amer. Chem. Soc. **98**, 6583 [1976].

[11] H. Mauser, loc. cit. 6a, p. 134.

[12] M. A. J. Rodgers and J. C. Becker, J. phys. Chem. **84**, 2762 (1980).

[13] U. Lachish, M. Otolenghi, and J. Rabani, J. Amer. Chem. Soc. **99**, 8062 (1977).

[14] D. Meisel, M. S. Matheson, and J. Rabani, J. Amer. Chem. Soc. **100**, 117 (1978).

[15] J. H. Baxendale and M. A. J. Rodgers, Chem. Phys. Lett. **72**, 424 (1980).

[16] N. Turro and A. Yekta, J. Amer. Chem. Soc. **100**, 5951 (1978); J. Coll. Int. Soc. **70**, 494 (1979).

[17] E. De Vendittis, Anal. Biochem. **115**, 278 (1981).

[18] R. Frank and H. Rau, unpublished.

[19] J. J. Grimaldi, S. Boileau, and J. M. Lehn, Nature London **265**, 229 (1977).

[20] H. Grätzel, K. Kalyanasundaram, and J. Kiwi, in Solar Energy Materials, Structure and Bonding **49**, Springer Verlag, Berlin 1982, p. 86p and literature cited.

[21] G. N. Schrauzer and U. Mayweg, J. Amer. Chem. Soc. **87**, 1483 (1965).

[22] M. F. Emerson and A. Holtzer, J. Phys. Chem. **71**, 1898 (1967).

[23] U. Hoffmann and A. Hofmann, "Einführung in die Optimierung", S. 178ff., Verlag Chemie, Weinheim 1971.