persion at the lower concentration of methanol due to the insufficient hydrophobicity.

For dilution of C_2H_5OH with nonpolar liquids, it is worth noting that the methylene bands (bands I and III) exhibited the frequency shifts but the methyl band (band II) did little, although such difference was not conspicuous for the mixing with polar liquids. This suggests that the CH_3 and CH_2 groups of ethanol are placed under different contacts with the surrounding molecules. It is also noted that $\Delta\nu_{AA}$ adopts positive values below $\chi_A \approx 0.3$, which appeared to be close to the concentration at which v_A changes its sign.[22] This feature was noted previously for the methanol/CCl_4 solution and confirmed for the ethanol/CCl_4 solution in this study. The rise of $\Delta\nu_{AA}$ around $\chi_A < 0.3$ would imply, if the discussion mentioned above were accepted, that the intermolecular distance (ethyl···ethyl) becomes larger as χ_A becomes smaller and accordingly suggests the formation of an assembly like a reversed micelle. Similar frequency shifts were observed by Amorim da Costa et al. for CTAB upon formation of a reversed micelle.[23]

In conclusion, the homogeneous and heterogeneous interaction factors obtained from the Raman difference analysis for the binary solutions seem to reflect a structural change of molecular association from the microscopic liquid phase to a cluster phase. This high sensitivity is probably attributed to the dependence of the C–H stretching frequencies on the dispersion force imposed on the probe molecule.

Registry No. C_2H_5OH, 64-17-5; CD_3CH_2OH, 1759-87-1; H_2O, 7732-18-5; CD_3OH, 1849-29-2; C_6D_6, 1076-43-3; CD_3CN, 2206-26-0; CCl_4, 56-23-5.

---

[22] Paraskevopoulos, G. C.; Missen, R. W. *Trans. Faraday Soc.* **1962**, *58*, 869.

[23] Amorim da Costa, A. M.; Geraldes, C. F. G. C.; Teixeira-Dias, J. J. C. *J. Colloid Interface Sci.* **1982**, *86*, 254.

Light-Induced Charge Separation by Formation of Insoluble Precipitates

Erich Walter Grabner* and Harald Hessberger

Institut für Physikalische und Theoretische Chemie der Universität Frankfurt, Niederurseler Hang, D-6000 Frankfurt am Main 51, Federal Republic of Germany *(Received: January 29, 1986; In Final Form: June 2, 1986)*

Preliminary experiments are reported on light-induced charge separation by quenching electronically excited species with formation of insoluble precipitates. Irradiation of acceptor–donor mixtures of 3-dimethylaminoperylene metaphosphate/tetramethyl-*p*-phenylenediamine (TMPD) and of Ag^+/perylene, respectively, in methylene chloride and with tetrabutylammonium perchlorate as supporting electrolyte formed precipitates of $TMPD^+ClO_4^-$ and Ag, respectively. The precipitates were separated from the solution by a platinum filter in a flow cell, which served as a simple battery for conversion of stored chemical energy into electrical energy. The quantum yield was about 10^{-6} and the battery voltage about 60 mV.

Introduction

There is much interest in processes for the conversion of light energy into chemical or electrical energy. For example, aromatic hydrocarbons in solution can be electronically excited by absorption of photons and subsequently quenched by suitable species.[1] In such quenching processes charge separation can occur leading to radical cations and anions.[2]

$$A^* + D \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A^{\bullet -} + D^{\bullet +} \qquad (1)$$

The efficiency of microscopic charge separation is usually very low because Coulombic attraction between the oppositely charged radical ions formed in the quenching process[3] leads to a large rate constant k_b of the back reaction of eq 1. However, this Coulombic attraction and therefore k_b should be substantially reduced if one of the precursors A or D bears an electrical charge, so that the products of the quenching process are a charged and an electrically *neutral* species.

$$A^{*+} + D \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} A + D^{\bullet +} \qquad (2)$$

This principle has been demonstrated by Tazuke et al.,[4] using quaternary ammonium ions based on the acceptor molecule benzophenone, and by Fendler et al.,[5] using Ag^+ ions as acceptors in the quenching of excited pyrene. In both cases the quenching reaction (eq 2) was driven to the right side as shown by the photochemical formation of crystal violet from leucocrystal violet and of colloidal Ag, respectively.

If one can obtain radical ions of sufficiently long life in the quenching process, it is possible to separate the photoproducts from the photolyzed solution. If one of the photoproducts is a solid, such as an insoluble radical cation salt, the separation can be accomplished by filtration.

$$D^{\bullet +} + S^- \rightarrow (D^{\bullet +}S^-)\downarrow \qquad (3)$$

Since the photoproducts formed according to eq 2 result from a charge separation process, the separated photoproducts (eq 3) should be electroactive and should be able to act as battery components in an electrochemical cell. Upon discharge, the original substances should be regenerated, allowing for cyclic operation of the device.

$$(D^{\bullet +}S^-) + A \rightarrow D + A^+ + S^- + \text{electrical energy} \qquad (4)$$

Accordingly, a system in which the steps of eq 2–4 take place efficiently should act as a cyclic system for energy conversion and storage. We here report preliminary results on two such systems that involve the formation of insoluble radical cation salts of tetramethyl-*p*-phenylenediamine (TMPD) with ClO_4^- ions in the aprotic solvents dimethoxyethane and methylene chloride[6] and the formation of colloidal Ag by quenching excited pyrene[5] or perylene. The colloidal Ag was coagulated by tetrabutylammonium perchlorate (TBAP) and was separated from the dissolved radical cations by filtration. The quantum yield in both systems was extremely low (ca. 10^{-6}).

---

[1] (a) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257. (b) Grellmann, K. H.; Watkins, A. R.; Weller, A. *J. Lumin.* **1970**, *1*, 678.

[2] Grellmann, K. H.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972**, *76*, 469, 3132.

[3] Mauzerall, D.; Ballard, S. G. *Annu. Rev. Phys. Chem.* **1983**, *33*, 377.

[4] Tazuke, S.; Kawasaki, Y.; Kitamura, N.; Inone, T. *Chem. Lett.* **1980**, 251.

[5] Jao, T.; Beddard, G. S.; Tundo, P.; Fendler, J. H. *J. Phys. Chem.* **1981**, *85*, 1963.

[6] Weller, A.; Zachariasse, K. *J. Chem Phys.* **1967**, *46*, 4984. Kotowski, S. Ph.D. Thesis, Frankfurt, 1978.

TABLE I: Electronic Excitation Energy, ΔE, and Standard Potential, $E°$, of Substances Chosen for Light-Induced Charge Separation by Fluorescence Quenching[h]

acceptor[g]	$\Delta E(^{1,3*}A)$/eV	$E°(A/A^{\bullet -})$/V vs. SCE	donor D	$\Delta E(^{1*}D)$/eV	$E°(D^{\bullet +}/D)$/V vs. SCE	$[E°(D^{\bullet +}/D) - E°(A/A^{\bullet -})]$/V vs. SCE
$TEAB^+$ (chloride)	3.01[a] (10)	−1.71[c] (11)	TMPD	3.52 (11)	0.16 (11)	1.87
			TPTA	3.51 (11)	0.74 (11)	2.45
			Pe	2.82[d] (12)	1.03 (7)	2.74
$DMAP^+$ (phosphate)	2.82[b] (12)	−1.72[c] (7)	TMPD	3.52 (11)	0.16 (11)	1.88
			TPTA	3.51 (11)	0.74 (11)	2.46
Ag^+		0.56 (13)	pyrene	3.33 (12)	1.16 (14)	3.2[e]
Cd^{2+}		−0.64 (13)				2.6[f]
Ag^+		0.56 (13)	Pe	2.82 (12)	1.03 (7)	3.07[e]
Cd^{2+}		−0.64 (13)				2.47[f]

[a] Triplet energy of benzophenone. [b] First excited singlet energy of perylene. [c] Potential of free aromatic substituents. [d] Sensitized species upon fluorescence quenching. [e] Accounting for the free energy of sublimation $\Delta G_s = 2.6$ eV. [f] Accounting for $\Delta G_s = 0.8$ eV. [g] $TEAB^+$: triethylammonium-4-methylenebenzophenone. $DMAP^+$: dimethylamino-3-perylene. TMPD: tetramethyl-*p*-phenylenediamine. TPTA: tri-*p*-tolylamine. Pe: perylene. [h] Numbers in parentheses are references.

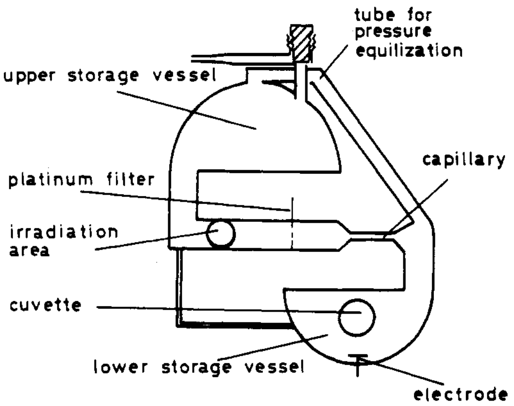

Figure 1. Flow cell for filtration of scarcely soluble precipitates formed by fluorescence quenching. The position shown corresponds to the irradiation stage; for filtration the cell is rotated by about 60° around an axis perpendicular to the drawing plane.

Experimental Section

Perylene (Pe), pyrene, tetramethyl-*p*-phenylenediamine (TMPD), tetrabutylammonium perchlorate (TBAP), and $AgClO_4$ (Fluka, p.a. quality) were used without further purification. Tri-*p*-tolylamine (TPTA)[7] and triethylammonium-4-methylenebenzophenone chloride ($TEAB^+Cl^-$)[4] were prepared by literature procedures. 3-Dimethylaminoperylene metaphosphate ($DMAP^+PO_3^-$) was prepared by nitration of perylene with HNO_3 to give 3-nitroperylene, reduction to the amine with hydrazine hydrate in methanol, and methylation with trimethyl phosphate.[8] $Cd(ClO_4)_2$ was obtained by mixing $CdCl_2 \cdot 2H_2O$ with $HClO_4$ and subsequent careful heating.

Solid compounds were freed from O_2 and H_2O by evacuation over P_2O_5. Solvents were dried by flowing through an Al_2O_3 column and subsequent distillation over P_2O_5 or B_2O_3 (acetonitrile). Oxygen was removed from the solutions by several freeze–pump–thaw cycles.

Preliminary experiments were conducted to determine what changes occurred on irradiation of the combinations chosen for study (Table I) and their components. Solutions of the components or systems were placed in a quartz cuvette, which could be evacuated, and irradiated with a high-pressure 200-W mercury lamp (30 min) or a Nd:YAG laser (5 min). Absorbance measurements in the cuvette were conducted with a two-beam spectrophotometer (Perkin-Elmer 555).

TABLE II: Photochemical Changes Caused by Irradiation of Donor/Acceptor Systems by a Mercury Lamp (30 min, $\lambda < 400$ nm) or a Nd:YAG Laser (5 min, $\lambda_{max} = 350$ nm) with Added Neutral Salt (TBAP, 0.5 M)[a]

system	solvent	remarks
$TEAB^+$/TMPD	AN	color change
$TEAB^+$/TPTA	AN	color change
$DMAP^+$/TMPD	MC	color change, after 2 days dark grey precipitate
$DMAP^+$/TMPD	AN	color change, little precipitate
$DMAP^+$/Pe	MC	color change
pyrene/Ag^+	methanol	color change, after 2 days precipitate
	AN	color change, dark grey precipitate
	DME	color change, little precipitate
pyrene/Cd^{2+}	methanol	color change
Pe/Ag^+	AN	color change, dark grey precipitate
	methanol	color change, precipitate
	DME	much precipitate
Pe/Cd^{2+}	AN	color change

[a] Concentration of donors and acceptors: 10^{-3}–10^{-2} M. AN = acetonitrile; MC = methylene chloride; DME = dimethoxyethane.

Experiments involving the separation of precipitates were carried out in a flow cell (Figure 1). The platinum filter (supplied by Degussa) was 11 mm in diameter with 1250 16-μm holes. The lower compartment contained a platinum wire electrode and optical windows for absorption measurements. The cell was placed in a Dewar vessel which could be kept at a constant temperature (±5 °C) between −100 and +50 °C. Flexible light cables were used for conduction of the radiation and for absorption measurements. The cell could be rotated around its horizontal axis so that precipitate could be deposited on the filter or solution could be returned from the lower to the upper storage. Experiments with the flow cell were performed with the mercury lamp and with an optical filter that cut off all wavelengths above 400 nm. The photon flux was determined with a calibrated thermopile (Kipp and Zonen). Absorption spectra were taken with a spectrofluorimeter MK-1 (Farrand) that was adapted to the geometry of the cell by means of light cables. A Wenking potentiostat TS 68 and a potential measuring device PPT 69 (Bank) were used for the electrochemical experiments.

Results

Irradiation in the Cuvette. The only system component that was affected in the preliminary cuvette experiments was TMPD in AN, which changed color. The absorption spectrum of the irradiated solution matched the reported absorption spectrum[9] of $TMPD^{\bullet +}$ radical cations. Irradiation of the donor–acceptor systems listed in Table I produced photochemical changes only with those listed in Table II.

The precipitate (0.15 mg) obtained upon irradiation of the system $DMAP^+$/TMPD was dissolved in AN (4 mL), and its absorption spectrum was compared with the absorption spectrum of $TMPD^+ClO_4^-$, prepared by oxidation of TMPD with oxygen (Figure 2). The peaks at 330 and 620 nm in the precipitate spectrum indicate that it is $TMPD^{\bullet +}$. In addition, the precipitate peak at 440 nm is attributed to perylene, presumably formed by decomposition of the radical $DMAP^\bullet$ or of $DMAP^+$. The pre-

---

(7) Grabner, E. W.; Brauer, E. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 106.

(8) We are indebted to the Institute of Organic Chemistry, University of Frankfurt, for this preparation.

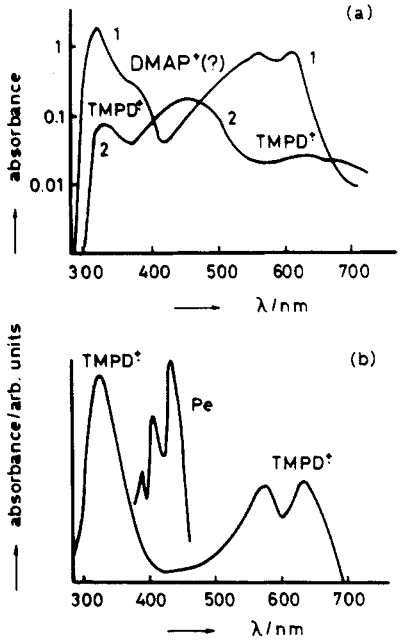

Figure 2. (a) Absorption spectra (in AN) of chemically prepared $TMPD^+ClO_4^-$ (curve 1) and of the precipitate formed by irradiation of the system $DMAP^+$/TMPD in MC (curve 2). (b) Absorption spectra of Pe in ethanol[15] and of $TMPD^{\bullet+}$ in 2-propanol.[9]

cipitates formed in the fluorescence quenching of perylene or pyrene by Ag^+ were dissolved in concentrated HNO_3. After dilution and addition of HCl a permanent turbidity was observed, indicating that the precipitates were elementary silver.

Experiments with the Flow Cell. The flow cell (Figure 1) was first checked to determine whether the filter was capable of filtering radical cation salts and whether the cell could operate as an electrochemical battery. For this purpose two additional Pt wires were sealed above and below the filter. A solution of perylene in methylene chloride (10^{-3} M) with TBAP (0.1 M) as supporting electrolyte was electrolyzed galvanostatically for 16 h (50 μA, 4–5 V). The upper Pt wire was the anode and the lower one the cathode. On subsequent cooling of the solution to about −75 °C a brownish violet precipitate of $Pe_2^+ClO_4^-$ formed near the anode.[6] The solution was then allowed to flow from the upper storage vessel into the lower one, depositing the precipitates on the filter. All these steps were controlled by measuring the voltage between the Pt filter and the lower Pt wire. The voltage was constant for a long period after cooling and flowing, indicating successful filtering and operation as a battery. However, discharge of the battery with currents of 0.1–0.5 μA caused a rapid decrease of the voltage due to (i) large contact resistance between the deposited radical cation salt and the Pt filter, (ii) large electrolytic resistance between the filter and the lower Pt electrode, and (iii) low concentration of radical anions near the lower electrode, impeding diffusion-controlled transport.

The donor–acceptor systems $DMAP^+$/TMPD and Pe/Ag^+ were then irradiated in the flow cell with the mercury lamp. In the system Pe/Ag^+ both the donor and the acceptor concentrations were 10^{-3} M in methylene chloride. In the system $DMAP^+$/TMPD the concentrations of the two components could not be made higher than 10^{-4} M because the solutions in methylene chloride became too viscous at higher concentrations at low temperatures. The concentration of the neutral salt TBAP was 0.5 M in both systems. The flow rate was 2 mL h^{-1} with $DMAP^+$/TMPD and 12–17 mL h^{-1} with Pe/Ag^+. The formation of precipitate was observed soon after starting the irradiation, which was continued for 6–7 h (Pe/Ag^+) or 50 h ($DMAP^+$/TMPD). After termination of the irradiation the precipitate was deposited on the filter by rotating the cell 60°.

At the end of the irradiation the voltage between the filter and the electrode in the lower storage vessel was 65 mV ($DMAP^+$/TMPD) or 30 mV (Pe/Ag^+). Whereas in the former case the filter electrode was positive, in the latter case it was negative.

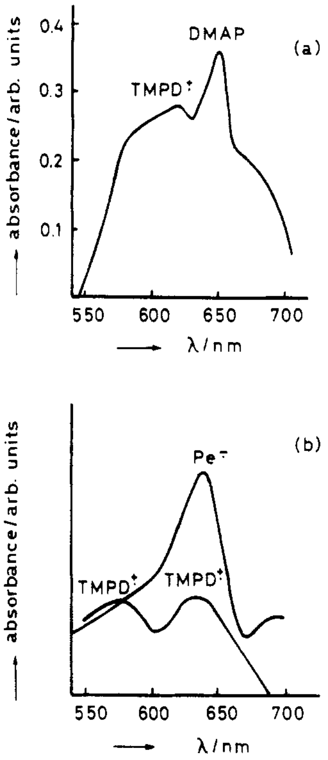

Figure 3. (a) Difference spectrum of the irradiated system $DMAP^+$/TMPD (10^{-4} M) in MC (with 0.5 M TBAP). (b) Absorption spectra of $TMPD^+$ in 2-propanol[9] and of $Pe^{\bullet-}$ in AN.[1]

When the two poles were connected by a resistance of 100 kΩ, a current of 0.1–0.5 μA flowed. In the system $DMAP^+$/TMPD this discharge could be maintained for several hours with a gradual decrease of the voltage to 2 mV. Renewed irradiation (after returning the solution from the lower to the upper storage) increased the voltage to 25–30 mV. Further discharge and irradiation yielded a voltage of 17–19 mV in the third cycle. The experiment was terminated after three cycles. In the system Pe/Ag^+ the cell could not be discharged for more than a few seconds because the voltage rapidly fell to 1 mV. After some hours at rest, however, the voltage recovered to 15–20 mV. When this system was irradiated at a lower temperature (−10 °C) where the radical cations are more stable, a cell voltage of 62 mV was measured.

Comparison of absorption spectra of the filtrates in the lower storage vessel (Figures 3a and 4a) with reported spectra (Figures 3b and 4b) suggested that $TMPD^{\bullet+}$ and $Pe^{\bullet-}$ were present in the system $DMAP^+$/TMPD, and $Pe^{\bullet+}$ in the system Pe/Ag^+. In the system Pe/Ag^+ a relatively large amount of Pe is present, whereas colloidal Ag is virtually absent. In Figure 3 ($DMAP^+$/TMPD) the absorbances at 632 and 640 nm are 0.329 and 0.446. With molar decadic absorption coefficients of 19 300 M^{-1} cm^{-1} for $TMPD^{\bullet+}$ at 632 nm[9] and of 51 000 M^{-1} cm^{-1} for $Pe^{\bullet+}$ at 640 nm,[15] and with an optical path of 2.5 cm, the concentrations of $TMPD^{\bullet+}$ and of $Pe^{\bullet-}$ are approximately 10^{-6} M.

The free-radical anion $Pe^{\bullet-}$ is probably not present in the filtrate, but rather the amine radical $DMAP^{\bullet}$ or a reaction product of it. However, the spectral characteristics of these species should be similar to that of $Pe^{\bullet-}$. In Figure 4 (Pe/Ag^+) there is seen a change of absorbance of 0.07 at 540 nm, indicating a $Pe^{\bullet+}$ concentration

---

(9) Meyer, W. C.; Albrecht, A. C. *J. Phys. Chem.* **1962**, *66*, 1168.

(10) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966; p 297.

(11) Zachariasse, K. A. Ph.D. Thesis, Amsterdam, 1972.

(12) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968; p 315.

(13) *Handbook of Chemistry and Physics*, 58th ed.; CRC: Cleveland, OH, 1977; D141, D67.

(14) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124.

(15) Leonhardt, H.; Weller, A. *Z. Phys. Chem.* (*Wiesbaden*) **1961**, *29*, 227; *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 791.

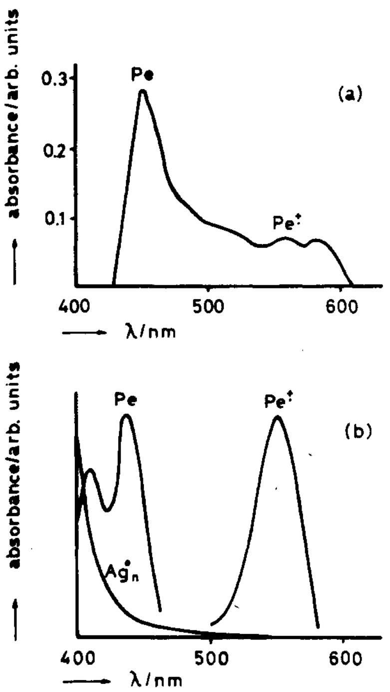

Figure 4. (a) Difference spectrum of the irradiated system Pe/Ag$^+$ (10^{-3} M) in MC (with 0.5 M TBAP). (b) Absorption spectra of Pe$^{\bullet+}$ in AN,[1] of Pe in ethanol,[15] and of colloidal Ag$_n^0$ in H_2O.[20]

of 5×10^{-8} M. This estimate is based on a molar decadic absorption coefficient of 63 000 M^{-1} cm^{-1} for Pe$^{\bullet+}$ at 540 nm.[2]

The voltage measured in the system Pe/Ag$^+$ at −10 °C (62 mV) is much smaller than that expected from considering the electrochemical cell Pt/Ag/Ag$^+$//Pe$^{\bullet-}$/Pe/Pt, which involves charge separation. With $c_{Ag^+} = c_{Pe} = 10^{-3}$ M and $c_{Pe^{\bullet+}} = 5 \times 10^{-8}$ M, a theoretical voltage of 390 mV was calculated for this cell. However, since only a fraction of the Ag$^+$ ions is converted to Ag, and consequently most of the Ag$^+$ ions pass the filter and reach the electrode in the lower storage vessel, these Ag$^+$ ions will control the potential at the Pe$^{\bullet+}$/Pe electrode, resulting in a mixed potential.

To confirm this assumption an experiment was performed to simulate the electrochemical situation in the flow cell. In a three-electrode cell a solution of 1.5 mM $AgClO_4$, 1.1 mM Pe, and 0.1 M TBAP in methylene chloride was galvanostatically electrolyzed to give a Pe$^{\bullet+}$ concentration of 10^{-7} M. The equilibrium potential between a Pt electrode and a Ag wire, both dipping into this solution, should be equivalent to the potential in the photochemical flow cell, and was about 120 mV.

The quantum yield of light-induced charge separation was estimated from the concentrations of radical ions in the filtrate (Figures 3 and 4) and from the photon flux of the mercury lamp (1.3×10^{17} photons cm^{-2} s^{-1} at $\lambda_{max} = 330$ nm). Thus, with a reaction volume of 100 mL, an irradiation area of 0.5 cm^2, and an irradiation time of 50 h (DMAP$^+$/TMPD) or 6 h (Pe/Ag$^+$), a quantum yield of 6×10^{-6} or 10^{-6} was estimated assuming complete absorption.

Discussion

Thermodynamics. The thermodynamic condition for the quenching process (eq 1 or 2) to yield radical cations and anions is that the free enthalpy of reaction be negative. This means that the energy of the excited donor, $\Delta E(D^*)$, or acceptor, $\Delta E(A^*)$, must be greater than the difference between the standard potential of oxidation of the donor to the corresponding radical cation, $E^\circ(D^{\bullet+}/D)$, and the standard potential of reduction of the acceptor to the corresponding radical anion, $E^\circ(A/A^{\bullet-})$

$$\Delta E(D^*, A^*) > e[E^\circ(D^{\bullet+}/D) - E^\circ(A/A^{\bullet-})] \tag{5}$$

where e = elementary electronic charge. The excited state can be the first excited singlet or the lowest triplet state, depending on the properties of the sensitizer–quencher system. In the case of fluorescence quenching by metal ions (e.g., Ag$^+$),[5] the free energy of sublimation ΔG_s must be added to the right-hand side of eq 5 because the primary photoproduct is not compact metal but single metal atoms or colloids.[16]

The systems studied for charge separation by quenching (Table I) were chosen so that eq 5 holds and so that the donors would form insoluble radical cation salts with ClO_4^- ions.

Kinetics. The following simplified kinetic scheme was used to estimate the quantum yield q of light-induced charge separation by quenching of excited species and formation of an insoluble precipitate. This scheme does not account for the peculiarities that arise when quanternary ammonium ions or metal ions are used as acceptors. Since kinetic data are not available for these species, and since the kinetics are aimed only at a rough estimate of the quantum yield, the simplification seems justified.

Absorption

$$A + h\nu \xrightarrow{k_1} A^* \tag{6}$$

Radiationless deactivation, fluorescence

$$A^* \xrightarrow{k_2} A + \text{energy} \tag{7}$$

Quenching

$$A^* + D \xrightarrow{k_3} (A^* \cdots D) \tag{8}$$

Deactivation of encounter complex

$$(A^* \cdots D) \xrightarrow{k_4} A + D + \text{energy} \tag{9}$$

Formation of radical ions

$$(A^* \cdots D) \xrightarrow{k_5} A^{\bullet-} + D^{\bullet+} \tag{10}$$

Recombination

$$A^{\bullet-} + D^{\bullet+} \xrightarrow{k_6} A + D \tag{11}$$

Formation of radical cation salt

$$D^{\bullet+} + S^- \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} (D^{\bullet+}S^-) \tag{12}$$

Nucleus formation

$$n(D^{\bullet+}S^-) \xrightarrow{k_8} (D^{\bullet+}S^-)_n \tag{13}$$

Crystal growth ($m \geqslant n$)

$$(D^{\bullet+}S^-) + (D^{\bullet+}S^-)_m \xrightarrow{k_9} (D^{\bullet+}S^-)_{m+1} \tag{14}$$

where n = size of the critical nucleus.

The formation of exciplexes from the encounter complex ($A^* \cdots D$) and the decomposition of exciplexes to give radical ions[17] are not considered separately but are included in reactions 8–10. The recombination of radical ions (eq 11) also includes the discharge of the radical cation salt.

$$A^{\bullet+} + (D^{\bullet+}S^-) \rightarrow A + D^- \tag{15}$$

Assuming photostationary conditions the following estimates can be made.[18] The efficiency of quenching (Φ_q) is given by the Stern–Volmer equation. From quenching experiments in the system perylene/diethylaniline,[1] which is similar to the systems used in this work, the quenching constant is approximately 10^2 M^{-1}. Our quenching experiments with the system DMAP$^+$/TMPD and perylene/Ag$^+$ yield quenching constants of 126 and 170 M^{-1}, respectively.[18] Hence Φ_q is approximately 0.5 at a donor concentration of 10^{-2} M. The efficiency Φ_i of formation of radical ions

$$\Phi_i = \frac{k_5}{k_4 + k_5} \tag{16}$$

---

(16) Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 556.
(17) Weller, A. *Z. Phys. Chem.* **1982**, *130*, 129.
(18) Hessberger, H. Ph.D. Thesis, Frankfurt, 1985.

is 0.5 for the favorable system pyrene/dimethylaniline in acetonitrile.[19] Experiments on the quenching of perylene with different quenchers in acetonitrile gave $\Phi_i = 0.1$ (with $k_4 = 4 \times 10^9$ s^{-1} and $k_5 = 6 \times 10^{10}$ s^{-1}).[1] Hence a value of $\Phi_i = 0.1$ seems to be reasonable for the systems studied in this work. The efficiency Φ_s of formation of a radical cation salt

$$\Phi_s = \frac{k_7 c_{S^-}}{k_6 c_{A\cdot^-} + k_7 c_{S^-}} \qquad (17)$$

where c_{S^-} and $c_{A\cdot^-}$ = concentration of S^- and $A^{\cdot -}$, respectively. is controlled by k_6 and by the concentrations c_{S^-} and $c_{A\cdot^-}$. Since k_6 is the rate constant k_b of eq 1, it is to be expected that $k_6 \gg k_7$. Nevertheless, once c_{S^-} is made sufficiently large by adding an inert salt ($c_{S^-} \simeq 1$ M), and since $c_{A\cdot^-}$ is usually very low (10^{-6} M), Φ_s should be approximately 1 even if k_6 is very large.

The quantum yield q is defined as the ratio of the number of radical cations (or metal atoms) being fixed as insoluble nuclei per second to the number of photons absorbed per second. It has been shown[18] that q can be expressed by

$$q = \Phi_q \Phi_i \Phi_s - \frac{K_s k_6 c_{A\cdot^-}}{I c_{S^-}} \qquad (18)$$

where I represents the photon flux and K_s the solubility product ($K_s = c_{D\cdot^+} c_{S^-}$) and where the following approximations are made: complete absorption and neglecting terms that include the very small concentrations of nuclei and crystallites.

The first term of the right-hand side of eq 18 is approximately 0.05, based on the estimates of Φ_q, Φ_i, and Φ_s above. Thus the maximum quantum yield should not exceed ca. 5%. The second term of the right-hand side of eq 18 reduces the maximum quantum yield and depends strongly on the solubility product K_s, on the light intensity I, and on the rate constant k_6 of the recombination reaction. With $K_s \simeq 10^{-9}$, derived from the solubility of $TMPD^+ClO_4^-$ in tetrahydrofuran,[6] and assuming this figure to be valid for the radical cation salts and solvents used in this work (preferentially methylene chloride), the second term in eq 18 is approximately 0.01. For this approximation $I = 10^{-5}$ einsteins/(dm^3 s), and k_6 and $c_{A\cdot^-}$ are 10^8 M^{-1} s^{-1} and 10^{-6} M, respectively. The value 10^{-6} M for $c_{A\cdot^-}$ was confirmed by experiment (see above).

These considerations show that if K_s and k_6 are small and I and c_{S^-} are large, the quantum yield q can attain a few percent. On the other hand, under less favorable conditions the second term of eq 18 can become the same order of magnitude as the first term, and the quantum yield should fall to an extremely low value.

It should be pointed out that Φ_i depends strongly on the polarity of the solvent, becoming larger with increasing polarity of the solvent. On the other hand, increasing polarity of the solvent increases the solubility of salts. Hence, a compromise must be found in the choice of a suitable solvent, which we sought by using the weakly polar solvent methylene chloride.

The discrepancy of approximately 4 orders of magnitude between the theoretically expected quantum yield (~0.05) and the observed quantum yield (~10^{-6}) can be understood by considering eq 18. The first term on the right-hand side, representing the maximum quantum yield of about 0.05, completely vanishes if the second term becomes equal to it. A value of $K_s = 10^{-9}$, based on the solubility of $TMPD^+ClO_4^-$ in THF,[6] was used for the theoretical estimate of q. However, the dielectric constant of THF (7.39) is somewhat smaller than that of methylene chloride (8.93), hence K_s is probably larger in the latter solvent than in the former. A difference in the solubility product of 1 order of magnitude suffices to make the first term vanish when all the other quantities of the second term are kept constant. It is therefore concluded that the relatively large solubility product of $TMPD^+ClO_4^-$ in methylene chloride is the main reason for the quantum yield being so small. On the other hand, the fact that a precipitate of $TMPD^+ClO_4^-$ is formed in the system $DMAP^+$/TMPD indicates that the rate constant k_6 of the back reaction is not large.

The quantum yield of the system Pe/Ag^+ is as low as that of the system $DMAP^+$/TMPD even though the solubility of metallic Ag is negligible. Accordingly, it appears that parameters other than K_s in the second term of eq 18 influence the value of q. It should be noted that a large light intensity can compensate for large K_s and k_6. Larger amounts of precipitate were observed in the experiments with the simple cuvette than in experiments in the flow cell; in the latter the light intensity was about 90% smaller than in the former. Accordingly, the quantum yield should be improved in an experimental arrangement that avoids the attenuation of light intensity by light cables.

The battery function of the flow cell depends mostly on the stability of the dissolved photoproducts $DMAP^\cdot$ and $Pe^{\cdot -}$, which is presumably not very high. The amine radical $DMAP^\cdot$ is formed by reduction of a tertiary ammonium ion instead of a quaternary ammonium ion as in the study of Tazuke et al.,[4] and it is possible that subsequent reactions like deprotonation take place. This may be the reason the battery function drastically decreased in only three cycles in the system $DMAP^+$/TMPD. Similarly, the perylene radical cations formed in the system Pe/Ag^+ are susceptible to reactions with nucleophiles,[6] which could explain the low concentration of $c_{Pe\cdot^+} \simeq 5 \times 10^{-8}$ M observed in this system. Moreover, it could be the reason for the low cell voltage (62 mV), which is only about half the voltage (120–150 mV) measured in the electrochemically simulated cell with $c_{Pe\cdot^+} = 10^{-7}$ M.

Acknowledgment. We are very indebted to Prof. Dr. W. Ried and Mrs. A. M. Normann for preparation of substances, and to Prof. Dr. H. D. Brauer for valuable discussions. Thanks are also due to the Deutsche Forschungsgemeinschaft for financial support.

Registry No. TMPD, 100-22-1; $TMPD^{\cdot +}$, 34527-55-4; Pe, 198-55-0; $Pe^{\cdot +}$, 12576-62-4; $Pe^{\cdot -}$, 34505-65-2; $DMAP^+PO_3^-$, 104465-53-4; TPTA, 1159-53-1; $TEAB^+Cl^-$, 69620-18-4; Ag, 7440-22-4; Ag^+, 14701-21-4; Cd^{2+}, 22537-48-0; pyrene, 129-00-0.

---

(19) Taniguchi, Y.; Mataga, N. *Chem. Phys. Lett.* **1972**, *13*, 596.

(20) Henglein, A.; Lindig, B.; Westerhausen, J. *J. Phys. Chem.* **1981**, *85*, 1627.