

# Photoinduced Energy and Electron Transfer between Ketone Triplets and Organic Dyes

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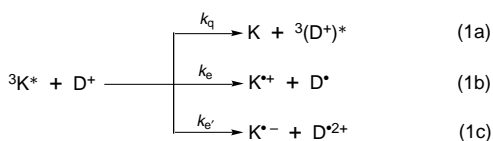
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Cationic organic dyes (phenosafranin, safranin T (ST<sup>+</sup>), thiopyronine, and methylene blue) are efficient quenchers of the triplet states of aromatic ketones. The triplets of benzophenone (BP), xanthone, thioxanthone, benzil, and *N*-methylacridone are quenched by the dyes via energy transfer, generating triplet excited dyes (typically  $k_q = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  ${}^3\text{BP}^* + \text{ST}^+$  in acetonitrile solution). Regarding Michler's ketone, *p*-(dimethylamino)benzophenone, and 3,6-bis(dimethylamino)thioxanthone, the mechanism of triplet quenching is solvent-dependent. Electron transfer occurs in polar solvents like acetonitrile, and energy transfer is the dominant reaction pathway in less polar solvents, such as dichloromethane. Delayed fluorescence of the dye caused by heterotriplet–triplet annihilation involving ketone and dye was detected upon studying the reaction of the dyes with triplet excited ketones (BP, xanthone, thioxanthone, and benzil). By applying two successive laser pulses ( $\lambda_{\text{ex}} = 532$  and 308 nm, respectively), the rate constant of the reaction  ${}^3\text{BP}^* + {}^3(\text{ST}^+)^*$  was determined:  $k_{\text{ht}} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

## 1. Introduction

Cationic organic dyes have received considerable attention in connection with commercial applications: They are employed, e.g., as laser dyes, dyes for textiles, and initiators for photopolymerization.<sup>1–3</sup> In many of these applications, the electronically excited triplet state of the dye is of particular importance. Mostly, however, the quantum yield of triplet formation is rather low, and therefore, triplet sensitizers are employed.

In this work, we report on the reaction of cationic organic dyes with certain ketones that frequently serve as triplet sensitizers. In this case, two photophysical pathways are possible, triplet–triplet energy transfer (eq 1a) or electron transfer (eqs 1b and 1c). The predominant pathway depends

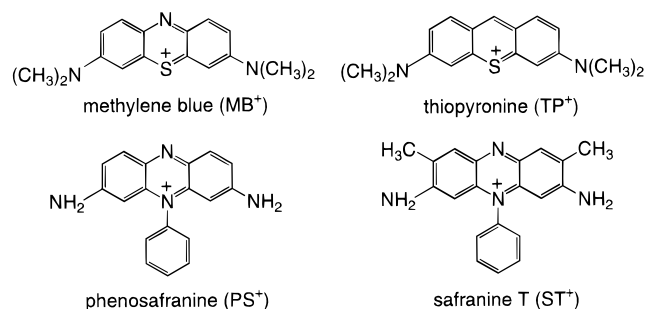


on the physical and photochemical properties of both dye and ketone. The structures of the cationic dyes used in this work are shown in Chart 1.

## 2. Experimental Section

**2.1. Materials.** Methylene blue (MB<sup>+</sup>Cl<sup>-</sup>) (Aldrich), phenosafranin (PS<sup>+</sup>Cl<sup>-</sup>) (Fluka), and safranin T (ST<sup>+</sup>Cl<sup>-</sup>) (Aldrich) were recrystallized from ethanol–water (4:1, v/v). Thiopyronine (TP<sup>+</sup>Cl<sup>-</sup>) (Fluka) was recrystallized 3 times from ethanol. Hydrogen chloride bonded to crystalline thiopyronine (TP<sup>+</sup>Cl<sup>-</sup> × 1/2HCl) was removed by heating at 100 °C *in vacuo* at 0.1 Torr.<sup>4</sup> Benzophenone (BP) (Aldrich) was purified with the aid of neutral Al<sub>2</sub>O<sub>3</sub> using *n*-hexane–ether (2:1, v/v) as eluent. Xanthone (X), thioxanthone (TX), benzil (BZ), *N*-

CHART 1: Structures of the Dyes



methylacridone (MAC), Michler's ketone (MK), and *p*-(dimethylamino)benzophenone (ABP) were recrystallized from ethanol and benzene. 3,6-Bis-(dimethylamino)thioxanthone (ATX) was synthesized as described in ref 5 and recrystallized 3 times from ethanol.

**2.2. Measurements.** Quantum yields of dye bleaching  $\Phi_{\text{dye}}$  were determined by continuous irradiation at 365 nm in a previously described setup<sup>6</sup> containing a high-pressure mercury lamp (HBO 200, Narva, Berlin) operated in conjunction with a metal interference filter (UVIF 365, Zeiss, Jena). The absorbed dose was determined by ferrioxalate actinometry.<sup>7,8</sup>

The excitation source utilized for flash photolysis studies was either a ruby laser operated in conjunction with a frequency doubler ( $\lambda_{\text{ex}} = 347$  nm; flash duration ca. 15 ns) or a frequency-doubled or -tripled Nd-YAG laser ( $\lambda_{\text{ex}} = 532$  and 355 nm, respectively; flash duration ca. 15 ns). Time-resolved emission spectra were recorded using an optical multichannel analyzer (Princeton Applied Research) with a 10-ns gate. The computer-controlled flash photolysis setup (Nd-YAG laser) has been described elsewhere.<sup>9</sup> Actinometry for  $\lambda_{\text{ex}} = 347$  and 355 nm was performed using the benzophenone/naphthalene triplet system.<sup>10</sup> Prior to irradiation, the solutions were bubbled with argon for 20 min in order to remove oxygen. Second-order rate constants were determined by laser flash photolysis (error limit:  $\pm 10\%$ ).

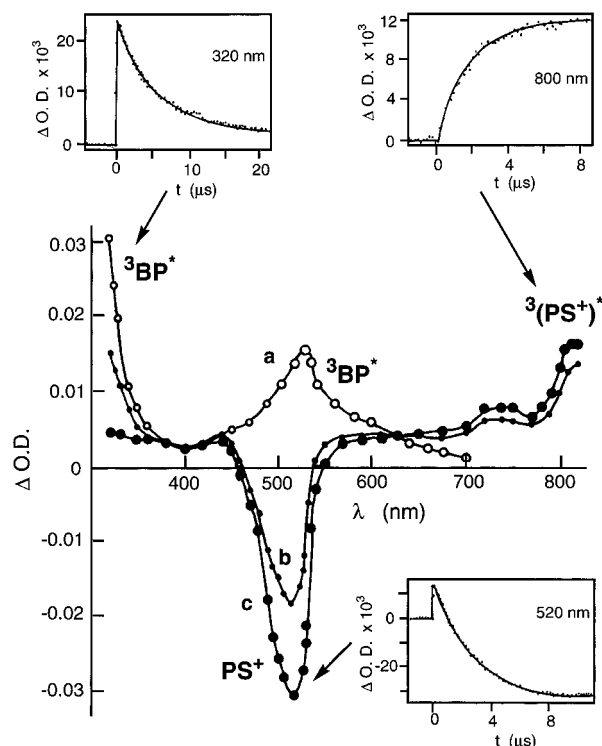
Redox potentials of the dyes were measured using a cyclic voltammeter (GWP 673 at 100 mV s<sup>-1</sup>) using platinum

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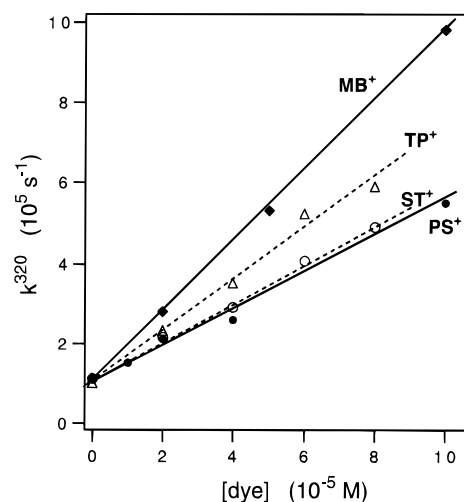
**Figure 1.** Transient optical absorption spectra recorded (a) at the end of the flash, (b) at 2.5  $\mu\text{s}$ , and (c) 10  $\mu\text{s}$  after irradiation of an argon-saturated acetonitrile solution containing BP ( $1 \times 10^{-3}$  M) and  $\text{PS}^+$  ( $4 \times 10^{-5}$  M) with a laser flash ( $\lambda_{\text{ex}} = 347$  nm;  $23^\circ\text{C}$ ;  $D_{\text{abs}} = 5 \times 10^{-6}$  einstein  $\text{L}^{-1}$ ). Insets: Kinetic traces recorded at different wavelengths following the laser flash ([BP] =  $1 \times 10^{-3}$  M; [ $\text{PS}^+$ ] =  $2 \times 10^{-5}$  M;  $D_{\text{abs}} = 6.2 \times 10^{-6}$  einstein  $\text{L}^{-1}$ ).

electrodes and SCE as reference. Tetrabutylammonium hexafluorophosphate (Fluka) was employed as the electrolyte for  $5 \times 10^{-4}$  M solutions of the dye in acetonitrile. Ferrocene served as the internal standard ( $E_{\text{ox}}^{\text{P}} = 0.42$  V SCE).<sup>11</sup>

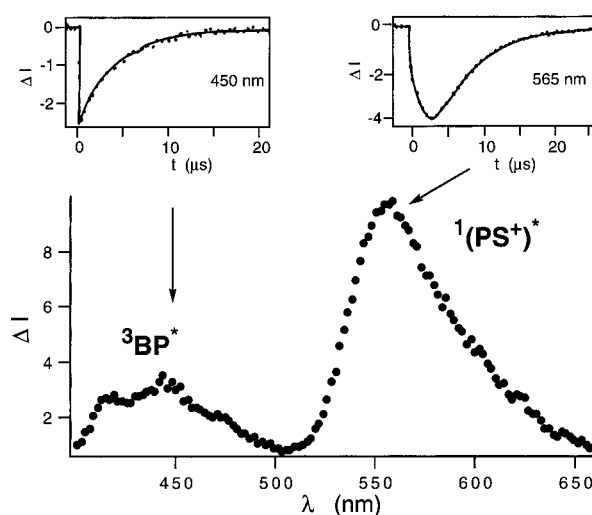
### 3. Results and Discussion

**3.1. Reaction of Ketone Triplets with  $\text{PS}^+$ . 3.1.1. The BP– $\text{PS}^+$  System.** Acetonitrile solutions containing BP and  $\text{PS}^+$  were irradiated at 347, 355, or 365 nm. At these wavelengths, the light is almost exclusively absorbed by BP. Continuous irradiation at  $\lambda_{\text{ex}} = 365$  nm resulted in a slight decrease in the  $\text{PS}^+$  concentration corresponding to a quantum yield of about 0.01. Interestingly, flash photolysis at  $\lambda_{\text{ex}} = 347$  nm revealed that BP triplets react effectively with  $\text{PS}^+$ . Transient optical absorption spectra recorded at various times after the laser flash are shown in Figure 1. The spectrum recorded at the end of the flash possesses strong absorptions at about 510 and 320 nm corresponding to BP triplets.<sup>12</sup> The ground-state absorption of  $\text{PS}^+$  ( $\lambda_{\text{max}} = 518$  nm) bleaches simultaneously with the decay of the BP triplet absorption at 320 nm. The bleaching process is paralleled by a buildup of a new absorption at 800 nm corresponding to  $^3(\text{PS}^+)^*$ .<sup>13</sup> Accordingly,  $^3\text{BP}^*$  is quenched by  $\text{PS}^+$  via triplet–triplet energy transfer (eq 1a). Furthermore, absorptions characteristic of redox intermediates of either reaction partner were not observed. Importantly, after a certain time, the absorption of ground-state  $\text{PS}^+$  is regenerated by a first-order process corresponding to a triplet lifetime  $\tau^3 = 25$   $\mu\text{s}$ , quite similar to the previously reported value.<sup>13</sup>  $k_{\text{q}}^{\text{BP}} = 5.5 \times 10^9$   $\text{M}^{-1} \text{s}^{-1}$ , the rate constant of the reaction  $^3\text{BP}^* + \text{PS}^+$ , was obtained by a pseudo-first-order kinetic treatment of the changes in the absorption of  $^3\text{BP}^*$  at 320 nm (Figure 2).

The emission spectrum recorded with the system BP/ $\text{PS}^+$  consists of three bands at 420, 450, and 555 nm (Figure 3).

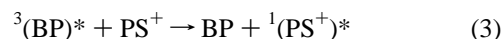
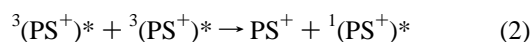


**Figure 2.** Pseudo-first-order rate constant of the  $^3\text{BP}^*$  decay at 320 nm vs the dye concentration ( $\text{PS}^+$ ,  $\text{ST}^+$ ,  $\text{TP}^+$ ,  $\text{MB}^+$ ; [BP] =  $1 \times 10^{-3}$  M;  $\lambda_{\text{ex}} = 347$  nm).



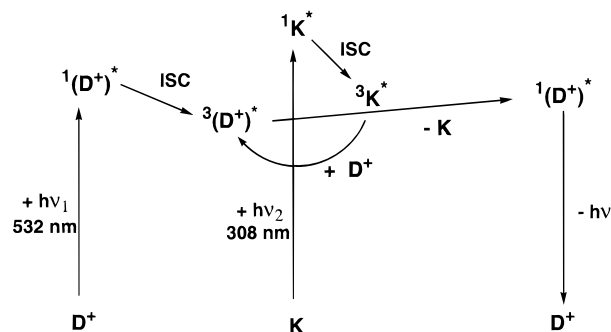
**Figure 3.** Transient optical emission spectra recorded 2  $\mu\text{s}$  after irradiation of an argon-saturated acetonitrile solution containing BP ( $1 \times 10^{-3}$  M) and  $\text{PS}^+$  ( $2 \times 10^{-5}$  M) with a laser flash ( $\lambda_{\text{ex}} = 355$  nm). Insets: Kinetic emission traces recorded at different wavelengths following the laser flash ( $\lambda_{\text{ex}} = 347$  nm;  $23^\circ\text{C}$ ;  $D_{\text{abs}} = 6.2 \times 10^{-6}$  einstein  $\text{L}^{-1}$ ).

The bands at 420 and 450 nm correspond to the phosphorescence of  $^3\text{BP}^*$ , which decays simultaneously with the absorption of  $^3\text{BP}^*$  at 320 nm (Figures 1 and 3). The band around 555 nm strongly resembles the steady-state fluorescence of  $\text{PS}^+$  in acetonitrile solution ( $\lambda_{\text{ex}} = 500$  nm), formed after the flash (see inset in Figure 3). Its decay is synchronous with the decay of  $^3\text{BP}^*$  and the bleaching of the dye (Figures 1 and 3). Therefore, the 555-nm band is attributed to “delayed fluorescence” emitted from  $^1(\text{PS}^+)^*$ , the excited singlet state of  $\text{PS}^+$ . Generally, three different mechanisms can be discussed regarding the origin of the delayed fluorescence in this case:



Accordingly,  $^1(\text{PS}^+)^*$  can be generated by homotriplet–triplet annihilation involving  $^3(\text{PS}^+)^*$  (eq 2), by triplet-to-singlet energy transfer from  $^3(\text{BP})^*$  to  $\text{PS}^+$  (eq 3), and by heterotriplet–triplet annihilation involving  $^3(\text{BP})^*$  and  $^3(\text{PS}^+)^*$  (eq 4). Provided that

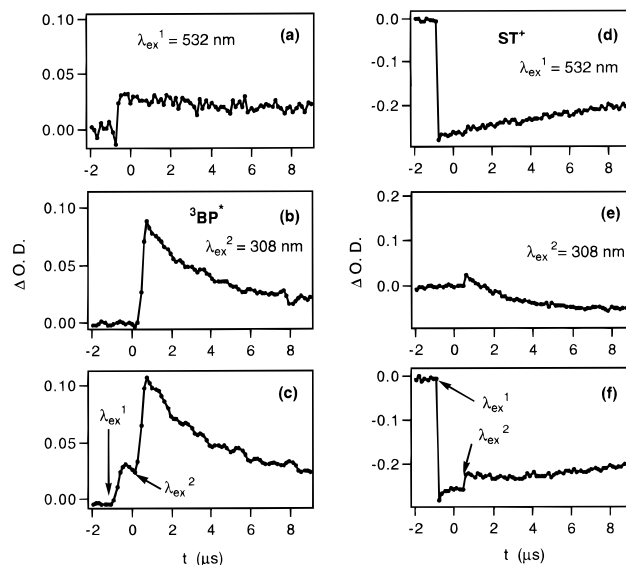
## SCHEME 1



delayed fluorescence originated from  $^1(\text{PS}^+)^*$ , formed according to eq 2, its decay should follow the decay of the optical absorption of  $^3(\text{PS}^+)^*$ . However, the lifetime of the delayed fluorescence was found to be much shorter than  $\tau = 25 \mu\text{s}$ , the lifetime of  $^3(\text{PS}^+)$ . Moreover, delayed fluorescence was not observed when  $^3(\text{PS}^+)^*$  was generated by irradiation of  $\text{PS}^+$  at  $\lambda_{\text{ex}} = 532 \text{ nm}$  in acetonitrile solution containing no other compound. Provided the mechanisms according to eq 3 or eq 4 would be operative, the decay rate of the delayed fluorescence should correspond to that of  $^3(\text{BP})^*$ , which was actually observed. To distinguish between these two mechanisms, the dependence of  $I_{\text{em}}$ , the intensity of light emitted at  $\lambda_{\text{em}} = 555 \text{ nm}$ , on  $I_{\text{ex}}$ , the intensity of the exciting light, was measured. In the case of triplet-to-singlet energy transfer,  $I_{\text{em}}$  should depend linearly on  $I_{\text{ex}}$  ( $I_{\text{em}} \propto I_{\text{ex}}$ ), and in the case of heterotriplet-triplet annihilation,  $I_{\text{em}}$  should depend exponentially on  $I_{\text{ex}}$  ( $I_{\text{em}} \propto I_{\text{ex}}^2$ ). The experimental results revealed an exponential dependence, and therefore, it was concluded that the delayed emission is caused by heterotriplet-triplet annihilation.

It is of particular interest to compare the reactions of  $^3(\text{BP})^*$  with  $\text{PS}^+$  in the ground state (eq 1a) and with  $\text{PS}^+$  in the triplet state (eq 4). To determine the rate constant of the latter reaction, the following *experiment* was carried out (see Scheme 1): A solution containing both BP and dye was at first irradiated with a 532-nm light flash to generate dye triplets and subsequently, delayed by  $1 \mu\text{s}$ , with an additional 308-nm light flash to generate benzophenone triplets. Such experiments require high-intensity laser pulses to convert sufficient ground-state molecules into the triplet state. Another prerequisite is a high quantum yield of triplet formation; i.e.,  $\Phi_{\text{isc}}$  must be large.  $\text{ST}^+$ , a derivative of  $\text{PS}^+$  (see Chart 1), undergoes intersystem crossing with a larger quantum yield than  $\text{PS}^+$ .<sup>14</sup> Since, moreover,  $\text{ST}^+$  exhibits a quenching behavior similar to that of  $\text{PS}^+$  ( $k_{\text{q}}^{\text{BP}}(\text{PS}^+) = k_{\text{q}}^{\text{BP}}(\text{ST}^+)$ ), it was chosen for these experiments. Ground-state  $\text{ST}^+$  was converted into the triplet state with a ca. 50% yield (Scheme 1). The exact degree of conversion was obtained from the change in the optical density at 520 nm (Figure 4d). The decay of  $^3(\text{BP})^*$  that also reacts with ground-state dye was monitored at 320 nm (Figure 4b). Typical kinetic traces illustrating the changes in the optical density both at 320 and 520 nm induced by irradiating a solution with pulses from both lasers are shown in Figure 4c and 4f. Because of the (weak) absorption of  $^3(\text{ST}^+)^*$  at 320 nm (Figure 4a), it was necessary to deconvolute the decay curves recorded at 320 nm (Figure 4c). Upon performing experiments at different  $\text{ST}^+$  concentrations with and without application of the pump pulse of 532-nm light and applying a pseudo-first-order kinetic treatment regarding the decay in the absorption at 320 nm, the bimolecular rate constant of the heterotriplet-triplet annihilation was determined with the aid of

$$k_{\text{exp}}^{320} = k_0 + k_{\text{q}}[\text{ST}^+] + k_{\text{ht}}[{}^3(\text{ST}^+)^*] \quad (5)$$



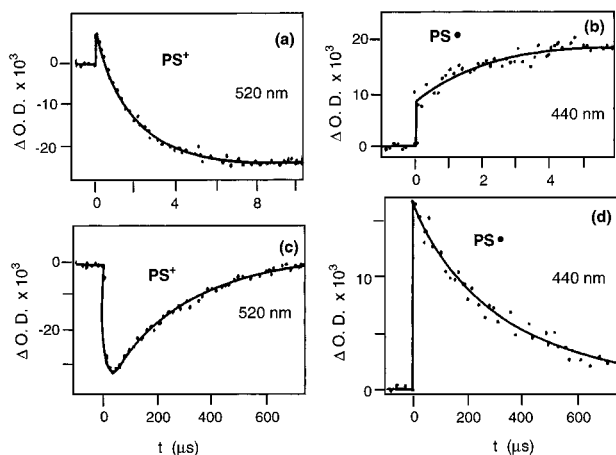
**Figure 4.** Double-laser experiment. Kinetic traces recorded at 320 nm (a–c) and 520 nm (d–f) following laser flash photolysis ( $\lambda_{\text{ex}}^1 = 532 \text{ nm}$ ;  $\lambda_{\text{ex}}^2 = 308 \text{ nm}$ ) of an argon-saturated acetonitrile solution containing BP ( $4 \times 10^{-3} \text{ M}$ ) and  $\text{ST}^+$  ( $2 \times 10^{-5} \text{ M}$ ).  $\lambda_{\text{ex}}^1 = 532 \text{ nm}$  (a, d);  $\lambda_{\text{ex}}^2 = 308 \text{ nm}$  (b, e); double-laser experiment,  $\lambda_{\text{ex}}^1 = 532 \text{ nm}$ ;  $\lambda_{\text{ex}}^2 = 308 \text{ nm}$ ; delay 1.2 ms (c, f).

where  $k_{\text{exp}}$  is the pseudo-first-order rate constant of the decay of the absorption at 320 nm obtained after deconvolution with respect of the absorption of  $^3(\text{ST}^+)^*$ ,  $k_0$  is the deactivation constant of  $^3(\text{BP})^*$  in the absence of the dye,  $k_{\text{q}}(\text{BP})$  is the bimolecular rate constant of quenching of  $^3(\text{BP})^*$  by ground-state dye, and  $k_{\text{ht}}$  is the bimolecular rate constant of the heterotriplet-triplet annihilation (eq 4). In this way,  $k_{\text{ht}} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  was determined. The high value indicates that the dye triplet is more reactive toward  $^3(\text{BP})^*$  than the dye singlet.

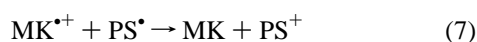
**3.1.2. The MK- $\text{PS}^+$  System.** The electronic characteristics of the triplet state of MK differ from that of BP. Because of its CT character,<sup>15,16</sup> triplet excited MK ( $^3(\text{MK})^*$ ) is prone to undergo electron-transfer reactions. Actually, flash photolysis of acetonitrile solutions containing both  $\text{PS}^+$  and MK at  $\lambda_{\text{ex}} = 347 \text{ nm}$  revealed that  $^3(\text{MK})^*$  reacts with  $\text{PS}^+$  via electron transfer (eq 1b) and not via energy transfer (eq 1a). Evidently,  $^3(\text{MK})^*$  reacts with  $\text{PS}^+$  much faster than  $^3(\text{BP})^*$ . A rather high rate constant ( $k_{\text{q}}(\text{MK}) = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), typical for electron transfer, was found by pseudo-first-order kinetic treatment of the ground-state bleaching of  $\text{PS}^+$  at  $\lambda_{\text{obs}} = 520 \text{ nm}$ , which follows synchronously the decay of the weak T-T absorption of MK at 650 nm. Typical kinetic traces recorded during the flash photolysis experiments are presented in Figure 5. Interestingly, a transient absorption at  $\lambda_{\text{obs}} = 800 \text{ nm}$  indicating the formation of  $^3(\text{PS}^+)^*$  was not detected. On the other hand, an absorption at  $\lambda_{\text{obs}} = 440 \text{ nm}$  attributed to  $\text{PS}^*$  radicals (the semireduced form of the dye<sup>13</sup>) grew in after the flash (see Figure 5b). The rate of the formation of the absorption at 440 nm (Figure 5b) corresponds to the rate of dye bleaching (Figure 5a) as expected on the basis of the occurrence of



The  $\text{PS}^*$  radical decayed, in the present case, with a half-life of about  $200 \mu\text{s}$ . As can be seen from the traces in Figure 5c and 5d, the absorption of ground-state  $\text{PS}^+$  recovers simultaneously with the decay of the absorption of  $\text{PS}^*$ , indicating the occurrence of back electron transfer

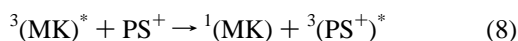


**Figure 5.** Kinetic traces recorded at different wavelengths following laser flash photolysis ( $\lambda_{\text{ex}} = 347$  nm;  $23$  °C;  $D_{\text{abs}} (10^{-6} \text{ einstein L}^{-1}) = 1.5$  (a, c),  $2.8$  (b, d)) of an argon-saturated acetonitrile solution containing MK ( $4 \times 10^{-6}$  M) and  $\text{PS}^+$  ( $4 \times 10^{-5}$  M).



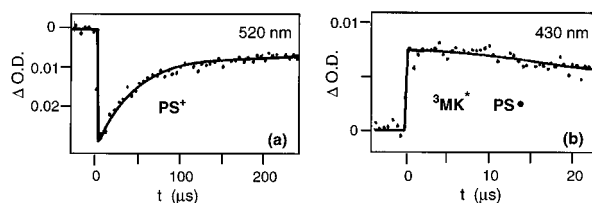
The remarkable photostability of the acetonitrile solution against continuous irradiation at 365 nm is in accordance with this result. The quantum yield of dye conversion is very low ( $\Phi_{\text{dye}} = 0.005$ ).

Notably, the mechanism of the reaction  ${}^3(\text{MK})^* + \text{PS}^+$  is solvent-dependent. Triplet-triplet energy transfer is the dominant reaction pathway when the reaction is performed in the less polar solvent dichloromethane ( $\epsilon_{\text{acetonitrile}} = 35.9$ ;  $\epsilon_{\text{dichloromethane}} = 8.9^{17}$ ). Flash photolysis experiments with dichloromethane solutions revealed that in this case, the absorption of  ${}^3(\text{PS}^+)^*$  at 800 nm is formed, indicating the occurrence of



The lifetime of  ${}^3(\text{PS}^+)^*$  is about  $25 \mu\text{s}$ . It is equal to the lifetime of the recovery of the ground-state absorption of  $\text{PS}^+$ . As can be seen from Figure 6a, the recovery is not quantitative. The trace approaches a saturation value definitely lower than zero, indicating the occurrence of a dye-consuming deactivation reaction. In this connection, it is noticeable that, in dichloromethane solution, also the formation of  $\text{PS}^{\bullet}$  was evidenced. The transient absorption at 430 nm (see kinetic trace in Figure 6b) contains, apart from the absorption attributed to  ${}^3(\text{MK})^*$ , also a portion attributed to the radical  $\text{PS}^{\bullet}$ . This suggests that electron transfer occurs in dichloromethane solution. The simultaneousness of the two deactivation reactions is also reflected by the magnitude of the rate constant of the quenching reaction  ${}^3(\text{MK})^* + \text{PS}^+$ .  $k_{\text{q}}(\text{MK}) = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in dichloromethane is lower than  $k_{\text{q}}(\text{MK}) = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in acetonitrile, but it is higher than  $k_{\text{q}}(\text{BP}) = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  measured for the reaction  ${}^3(\text{BP})^* + \text{PS}^+$  in acetonitrile, which solely involves energy transfer.

**3.1.3. Other Ketones.** The results concerning the reaction of  $\text{PS}^+$  with various other ketones in the excited triplet state are summarized in Table 2. Electron transfer was observed only with MK and ABP in the strongly polar solvent acetonitrile. In the cases of the other ketones, triplet quenching occurs via energy transfer with rate constants ranging from  $5.5 \times 10^9$  to  $7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The slightly higher rate constant measured in the case of ATX indicates a contribution of electron transfer. Notably,  ${}^3\text{ATX}^*$  reacts with  $\text{PS}^+$  exclusively via electron transfer in propylene carbonate (PC), a solvent more polar than acetonitrile ( $\epsilon_{\text{PC}} = 65^{18}$ ). The rate constant  $k_{\text{e}}^{\text{ATX}} = 1.4 \times 10^9$



**Figure 6.** Kinetic traces recorded at different wavelengths following laser flash photolysis ( $\lambda_{\text{ex}} = 347$  nm;  $23$  °C;  $D_{\text{abs}} = 3 \times 10^{-6} \text{ einstein L}^{-1}$ ) of an argon-saturated dichloromethane solution containing MK ( $4 \times 10^{-6}$  M) and  $\text{PS}^+$  ( $4 \times 10^{-5}$  M).

**TABLE 1: Characterization of Dye Cations<sup>a</sup>**

	$\text{PS}^+$	$\text{ST}^+$	$\text{TP}^+$	$\text{MB}^+$
$E^{\text{S}}$ , eV	2.34 <sup>b</sup>	2.36 <sup>b</sup>	2.21 <sup>b</sup>	1.89 <sup>b</sup>
$E^{\text{T}}$ , eV	1.77 <sup>c</sup>	1.78 <sup>b</sup>	1.80 <sup>d</sup>	1.50 <sup>b</sup>
$E_{\text{red}}^{1/2}$ , eV	-0.66 <sup>e</sup>		-0.64 <sup>e</sup>	-0.36 <sup>e</sup>
${}^3\tau$	25 <sup>f</sup>		80 <sup>e</sup>	36 <sup>g</sup>
$k_{\text{q}}^{\text{BP}} 10^9 \text{ M}^{-1} \text{ s}^{-1}$	5.5	5.5	6.7	8.5

<sup>a</sup>  $E^{\text{S}}$ : singlet energy.  $E^{\text{T}}$ : triplet energy.  $E_{\text{red}}^{1/2}$ : reduction potential (SCE).  ${}^3\tau$ : triplet lifetime.  $k$ : rate constant of the reaction  ${}^3\text{BP}^* + \text{dye}$  in acetonitrile. <sup>b</sup> Reference 14. <sup>c</sup> Reference 22. <sup>d</sup> Reference 4. <sup>e</sup> Measured in this work. <sup>f</sup> Reference 23. <sup>g</sup> Reference 20.

**TABLE 2: Characterization of Ketones**

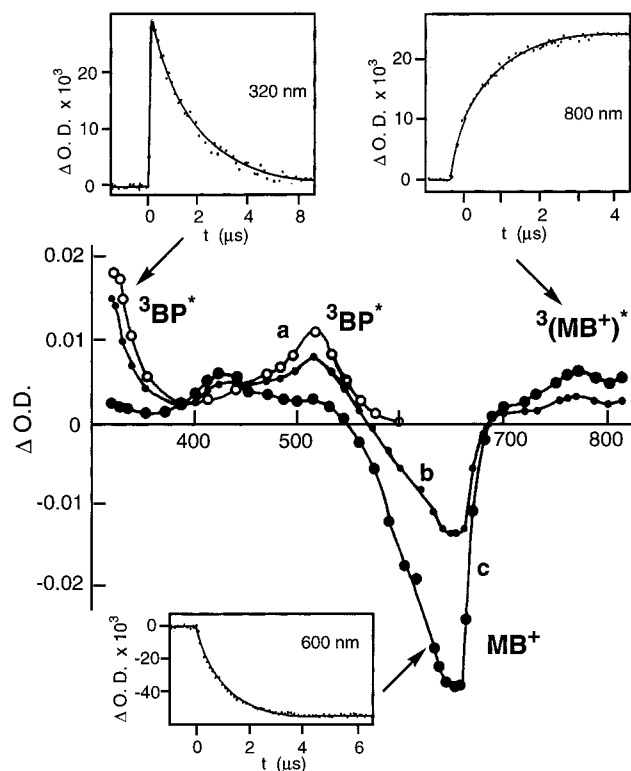
ketone	$E^{\text{T}}$ , eV	$E_{\text{ox}}^{1/2}$ , V	$\Delta_{\text{R}}G^{\text{,b}}$ eV	$k, 10^9 \text{ m}^{-1} \text{ s}^{-1}$		
				CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	<i>I</i>
BP	3.0 <sup>c</sup>	2.39 <sup>g</sup>	0.05	5.5 q		1.0
X	3.2 <sup>c</sup>	1.8 <sup>g</sup>	-0.74	7.4 q		0.6
TX	2.8 <sup>c</sup>	1.69 <sup>g</sup>	-0.45	6.2 q		0.45
BZ	2.4 <sup>d</sup>	2.0 <sup>h</sup>	0.26	5.8 q		0.3
MAC	2.6 <sup>c</sup>	1.47 <sup>i</sup>	-0.47	5.4 q		0.0
ABP	2.7 <sup>e</sup>	1.08 <sup>i</sup>	-0.96	12 e	9 q,e	0.0
MK	2.7 <sup>c</sup>	0.95 <sup>i</sup>	-1.09	13 e	8.7 q,e	0.0
ATX	2.7 <sup>f</sup>	1.10 <sup>i</sup>	-0.94	8.7 e,q		0.0

<sup>a</sup>  $E^{\text{T}}$ : triplet energy.  $E_{\text{ox}}^{1/2}$ : oxidation potential (SCE).  $\Delta_{\text{R}}G$ : free reaction enthalpy for reduction of  $\text{PS}^+$  by ketone triplets.  $k$ : rate constant of the reaction of  $\text{PS}^+$  + ketone triplets in acetonitrile and dichloromethane. q: dominant energy transfer. e: electron transfer. q,e: energy and electron transfer equally important. *I*: relative intensity of the delayed fluorescence of  $\text{PS}^+$  (normalized to BP). <sup>b</sup> Calculated by  $\Delta_{\text{R}}G = E_{\text{ox}}^{1/2}(\text{ketone}) - E_{\text{red}}^{1/2}(\text{PS}^+) - E^{\text{T}}(\text{ketone})$ . <sup>c</sup> Reference 24. <sup>d</sup> Reference 25. <sup>e</sup> Reference 26. <sup>f</sup> Determined from the phosphorescence spectrum at 77 K in ether/ethanol/toluene glass. <sup>g</sup> Reference 5. <sup>h</sup> Reference 27. <sup>i</sup> Measured in this work.

$\text{M}^{-1} \text{ s}^{-1}$  measured in PC is lower than  $k_{\text{e}}^{\text{MK}}$  and  $k_{\text{e}}^{\text{ABP}}$  measured in acetonitrile because of the higher viscosity of this solvent ( $\eta_{\text{PC}} = 2.53 \text{ cP}^{19}$ ;  $\eta_{\text{acetonitrile}} = 0.36 \text{ cP}^{17}$ ).

Hetero-T-T annihilation, evidenced by delayed fluorescence of  $\text{PS}^+$ , was only found with solutions containing BP, X, TX, or BZ. Obviously, only the triplets of these ketones are capable of reacting with  $\text{PS}^+$  triplets. So far, it has not been elucidated why triplets of the other ketones examined in this work do not undergo hetero-T-T annihilation. A straightforward correlation of the aptitude to this reaction and the triplet energy of the ketones could not be established. Actually, such a correlation seems feasible on the basis of the fact that in the cases of several ketones (BP, X, TX, BZ), the relative intensity of the delayed fluorescence decreases in the same order, namely,  $I(\text{BP}) > I(\text{X}) > I(\text{TX}) > I(\text{BZ})$ , as the triplet energy:  $E^{\text{T}}(\text{BP}) > E^{\text{T}}(\text{X}) > E^{\text{T}}(\text{TX}) > E^{\text{T}}(\text{BZ})$ . However, in the cases of other ketones (MAC, ABP, MK) possessing triplet energies higher than that of BZ, delayed fluorescence is not observed at all.

**3.2. Reaction of Ketone Triplets with  $\text{MB}^+$ .** Low quantum yields of dye bleaching ( $\Phi_{\text{MB}}^{\text{BP}} = 0.004$  and  $\Phi_{\text{MB}}^{\text{MK}} = 0.015$ ) were obtained upon continuous irradiation of ketones at 365

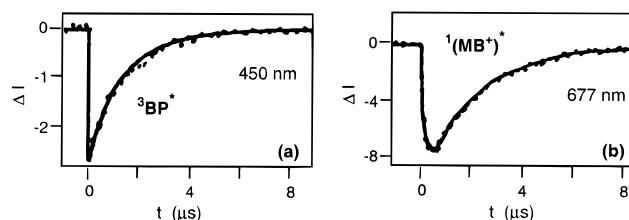


**Figure 7.** Transient optical absorption spectra recorded (a) at the end of the flash, (b) at 0.3  $\mu\text{s}$ , and (c) 10  $\mu\text{s}$  after irradiation of an argon-saturated acetonitrile solution containing BP ( $1 \times 10^{-3}$  M) and MB $^+$  ( $2 \times 10^{-5}$  M) with a laser flash ( $\lambda_{\text{ex}} = 347$  nm; 23  $^{\circ}\text{C}$ ;  $D_{\text{abs}} = 4 \times 10^{-6}$  einstein L $^{-1}$ ). Insets: Kinetic traces recorded at different wavelengths following the laser flash ([BP] =  $1 \times 10^{-3}$  M; [MB $^+$ ] =  $5 \times 10^{-5}$  M;  $D_{\text{abs}} = 5.7 \times 10^{-6}$  einstein L $^{-1}$ ).

nm in Ar-saturated acetonitrile solutions containing BP or MK, respectively.

Laser flash photolysis experiments at  $\lambda_{\text{ex}} = 347$  nm revealed results similar to those found in the case of PS $^+$ /ketone systems. Since MB $^+$  possesses a more positive reduction potential than PS $^+$  (Table 1), the reaction enthalpy of the reduction of the dye by ketone triplets, calculated with the aid of the Rehm–Weller equation, is more negative. Consequently, electron transfer was expected to be the favorable reaction mode. However, in comparing the reaction of MB $^+$  and PS $^+$  with ketone triplets, only marginal differences regarding the competition between energy and electron transfer were detected. The ketones examined in this case were BP, MAC, MK, and ATX. In acetonitrile solution, energy transfer was observed for the reaction of MB $^+$  with  $^3\text{BP}^*$  and  $^3\text{MAC}^*$  and electron transfer for the reaction MB $^+$  +  $^3\text{MK}^*$ . Both reaction pathways seem to be involved in the reaction MB $^+$  +  $^3\text{ATX}^*$ . In analogy to the system PS $^+$ /MK, the mode of the reaction pathway changed from electron transfer to energy transfer when the reaction MB $^+$  +  $^3\text{MK}^*$  was performed in dichloromethane instead of acetonitrile.

Typical results concerning the system MB $^+$ /BP are presented in Figure 7, where transient absorption spectra recorded at various times after the 15-ns flash are shown. The absorption bands at 320 and 510 nm, which are formed during the flash, are attributed to  $^3\text{BP}^*$ . The absorption of  $^3\text{BP}^*$  decreases simultaneously with the bleaching of the ground-state absorption of MB $^+$  (around 600 nm) and the growth of the T–T absorption of  $^3(\text{MB}^+)^*$  at 800 nm.<sup>20</sup> The kinetic traces, shown as insets in Figure 7, demonstrate the simultaneousness of these processes. The formation of the absorption of  $^3(\text{MB}^+)^*$  suggests the occurrence of energy transfer (eq 1a). Obviously, absorptions



**Figure 8.** Kinetic emission traces recorded at different wavelengths following laser flash photolysis ( $\lambda_{\text{ex}} = 347$  nm; 23  $^{\circ}\text{C}$ ;  $D_{\text{abs}} = 6 \times 10^{-6}$  einstein L $^{-1}$ ) of an argon-saturated dichloromethane solution containing BP ( $1 \times 10^{-3}$  M) and MB $^+$  ( $5 \times 10^{-5}$  M).

due to redox intermediates were not observed. Importantly, the initial absorption of MB $^+$  is regenerated within about 35  $\mu\text{s}$  (not shown in Figure 7). In this connection, it is notable that a triplet lifetime of similar magnitude was found for  $^3(\text{MB}^+)^*$  by Kamat and Lichtin.<sup>20</sup> The recovery of the ground-state absorption of MB $^+$  shows that irreversible processes leading to permanent dye bleaching do not occur. Pseudo-first-order kinetic treatment of the changes in the absorption of  $^3\text{BP}^*$  yielded the rate constant of the reaction  $^3\text{BP}^* + \text{MB}^+$ :  $k_{\text{d}}^{\text{BP}} = 8.5 \times 10^9$  M $^{-1}$  s $^{-1}$ . This rate constant is only slightly larger than that of the reaction  $^3\text{BP}^* + \text{PS}^+$  (Table 2).

The rate constant of the reaction  $^3\text{MAC}^* + \text{MB}^+$  could not be determined because the absorptions of  $^3\text{MAC}^*$  and MB $^+$  (ground state) are strongly overlapping. But the appearance of the absorption of  $^3(\text{MB}^+)^*$  at 770 nm confirms the energy-transfer mechanism concerning the reaction  $^3\text{MAC}^* + \text{MB}^+$ . The reaction  $^3\text{MK}^* + \text{MB}^+$ , on the other hand, proceeds via electron transfer (in acetonitrile solution). The rate constant is high:  $k_{\text{e}}^{\text{MK}} = 1.5 \times 10^{10}$  M $^{-1}$  s $^{-1}$ . MB $^+$ , generated by this reaction, was evidenced by its characteristic absorption at 430 nm.<sup>20</sup> On the other hand,  $^3(\text{MB}^+)^*$ , which should be formed by energy transfer, was not detected in this case.

In analogy to the PS $^+$ /MK system dealt with in section 3.1.2, the mode of reaction pathway (electron or energy transfer) is expected to be influenced by solvent polarity. It turned out that in the weakly polar solvent dichloromethane, the reaction  $^3\text{MK}^* + \text{MB}^+$  proceeds predominantly via energy transfer as was evidenced by the formation of  $^3\text{MK}^*$ , detected by its characteristic absorption at 770 nm. Moreover, a rather strong absorption at 430 nm due to MB $^+$  was observed, indicating that electron transfer also occurs. Apparently, the partitioning is in favor of electron transfer in the present case. In this respect, the MB $^+$ /MK system differs from the PS $^+$ /MK system where the energy transfer pathway is favored in dichloromethane. The difference probably reflects differences in the reduction potential, which in the case of MB $^+$  is somewhat more positive than that of PS $^+$  (see Table 1).

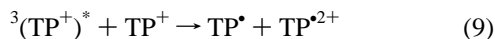
Heterotriplet–triplet annihilation, according to eq 4, was also observed with the system BP/MB $^+$ : as is seen from kinetic trace b in Figure 8, delayed fluorescence originating from reaction  $^3\text{BP}^* + ^3(\text{MB}^+)^*$  is emitted from  $^1(\text{MB}^+)^*$  at 677 nm. The emission at 450 nm (trace a in Figure 8) is due to the phosphorescence of  $^3\text{BP}^*$ .

**3.3. Reaction of Ketone Triplets with TP $^+$ .** TP $^+$  possesses photophysical properties similar to those of PS $^+$  and MB $^+$  (Table 1), which suggests also that its reactivity toward ketone triplets should be similar. This was confirmed by laser flash photolysis experiments at  $\lambda_{\text{ex}} = 347$  nm. It turned out, for example, that TP $^+$ , in analogy to PS $^+$  and MB $^+$ , reacts with  $^3\text{BP}^*$  via triplet–triplet energy transfer. Moreover, delayed fluorescence was emitted from  $^1(\text{TP}^+)^*$ , thus demonstrating the occurrence of heterotriplet–triplet annihilation also in this case.

Different reaction pathways were observed for the reaction  $^3\text{MK}^* + \text{TP}^+$  in acetonitrile and dichloromethane solution. In

polar acetonitrile,  ${}^3\text{MK}^*$  is quenched via electron transfer ( $k_e^{\text{MK}} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and in less polar dichloromethane by energy transfer ( $k_q^{\text{MK}} = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). (Detailed information concerning these results is contained in the supporting material.)

Upon continuous irradiation of BP/TP<sup>+</sup> in acetonitrile solutions at  $\lambda_{\text{ex}} = 365 \text{ nm}$ , a rather high quantum yield of dye conversion was found:  $\Phi_{\text{TP}^{\text{BP}}} = 0.1$ . The fact that this value is much higher than comparable values ( $\Phi_{\text{MB}^{\text{BP}}} = 0.004$  and  $\Phi_{\text{PS}^{\text{BP}}} = 0.01$ ) very likely reflects the high probability of the occurrence of reaction 9, i.e., the reaction of  ${}^3(\text{TP}^+)^*$  with ground-state dye



By this disproportionation reaction ( $k_{\text{sq}} = 7.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>21</sup> semireduced and semioxidized dye is formed <sup>4</sup>.

Notably, the rate constants of the corresponding reactions of  ${}^3(\text{PS}^+)^*$  and  ${}^3(\text{MB}^+)^*$  are lower ( $k_{\text{sq}}^{\text{MB}} = 3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>20</sup>. Moreover, the lifetimes of  ${}^3(\text{PS}^+)^*$  and  ${}^3(\text{MB}^+)^*$  are shorter than that of  ${}^3(\text{TP}^+)^*$  (Table 1). Therefore, in these cases, the triplets deactivate almost quantitatively to the ground state and the quantum yield of dye conversion at continuous irradiation is quite low (see above).

#### 4. Conclusions

Heteroanthracene-type dyes, such as PS<sup>+</sup>, TP<sup>+</sup>, and MB<sup>+</sup>, effectively quench the triplet states of the aromatic ketones BP, X, TX, BZ, and MAC by energy transfer, and thereby, triplet excited dyes are formed. The triplet states of other ketones (MK, ABP, and ATX) can be quenched by the dyes also via an electron-transfer mechanism. It turned out that the mode of reaction pathway strongly depends on the solvent polarity. Whereas electron transfer is favored in polar solvents like acetonitrile, energy transfer is the dominant reaction pathway in less polar solvents such as dichloromethane. Generally, the rate constant of electron transfer is larger than that of energy transfer.

Heterotriplet–triplet annihilation occurs in the reaction of triplet excited dyes with triplet excited ketones in several cases (BP, X, TX, BZ). This process gives rise to delayed fluorescence of the dye which can be readily detected by time-resolved luminescence measurements. Moreover, it was found that dyes in the excited triplet state are more reactive toward triplet excited ketones than in the excited singlet state.

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**Supporting Information Available:** A detailed description of laser flash photolysis results for the reaction of ketone triplets with TP<sup>+</sup> along with figures (5 pages). Ordering information is given on any current masthead page.

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