

## 51. Photoinduced Electron-Transfer Reactions of Perylene in Acetonitrile

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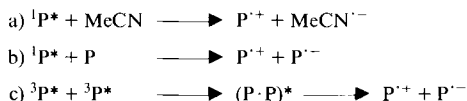
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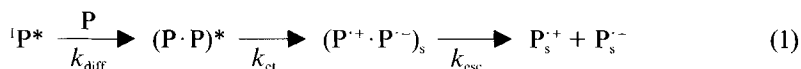
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Laser-flash-photolysis experiments show that, in MeCN at 20°, perylene (P) undergoes three distinct electron-transfer reactions:

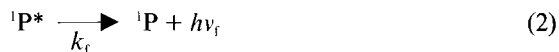


These processes originate probably from the thermally relaxed excited states of P.

**Introduction.** – The photoinduced electron-transfer processes of perylene (P) in polar solvents have been the object of several investigations [1–3] which have led to contradictory conclusions. It is established that in flash-photolysis experiments both radical ions  $\text{P}^{'+}$  and  $\text{P}^{\prime-}$  are formed in MeCN, and this was attributed to electron transfer within the excimer or collision complex according to *Eqn. 1*.



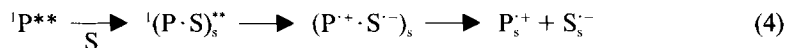
Here,  $(\text{P}\cdot\text{P})^*$  refers to an excimer or collision complex of indeterminate multiplicity,  $(\text{P}^{'+}\cdot\text{P}^{\prime-})_s$  to the solvated contact ion pair and  $\text{P}_s^{'+}$ ,  $\text{P}_s^{\prime-}$  to the separated, solvated ions. Such a mechanism implies that the reactive state  ${}^1\text{P}^*$  is the thermally equilibrated singlet excited state of P and that the electron-transfer process is, therefore, in competition with the deactivation of  ${}^1\text{P}^*$  by fluorescence and intersystem crossing:



The validity of *Eqn. 1* was subsequently questioned on the basis of quenching experiments: 0.8M PhBr was reported to quench the fluorescence of P without affecting the ion yield [2] and this observation would indeed rule out the relaxed excited states  ${}^1\text{P}^*$  or  ${}^3\text{P}^*$  as precursors in the electron-transfer reaction.

On the basis of this and similar observations a general mechanism of photoionization of aromatic molecules in liquid solvents was proposed [2]. Ionization is seen as an electron

transfer from a *non-relaxed*<sup>1)</sup> excited molecule  ${}^1P^{**}$  to the solvent S, through some charge-transfer-to-solvent state akin to a *Rydberg* state in which the excited electron is delocalized over the solvation shell of the solute molecule:



Obviously, this process would lead to the solute radical cation  $P^+$  and to the solvated electron (or solvent radical anion), and it is difficult to see how it could form the solute positive *and* negative radical ions simultaneously. Electron capture from  $S_s^-$  by ground state P to produce  $P^-$  has been suggested recently [3] although no build-up of  $P^-$  could be detected at  $[P] \approx 10^{-4}$  M. Here, we report a detailed investigation of the P/MeCN system by laser flash photolysis using absorption and emission spectrophotometric detection as well as transient photocurrent measurements. On the basis of all available evidence a complete scheme for the electron-transfer reactions of P in MeCN can be constructed.

**Results.** - When a  $2.8 \times 10^{-4}$  M deoxygenated solution of P in MeCN is irradiated with a 25-ns laser pulse at 355 nm, transient absorptions attributable to the radical ions  $P^+$  and  $P^-$  and to the triplet  ${}^3P^*$  are observed (*Fig. 1a*). The initial absorptions vary linearly with the absorbed laser-light intensity over a five-fold decrease (*Fig. 1b*).

At short times, the ion absorptions show a small rise up to  $\sim 400$  ns. This rise disappears in aerated or  $O_2$ -saturated solutions but the radical cation  $P^+$  is still formed during the 25-ns flash albeit with a slightly lower yield (*Fig. 2*).

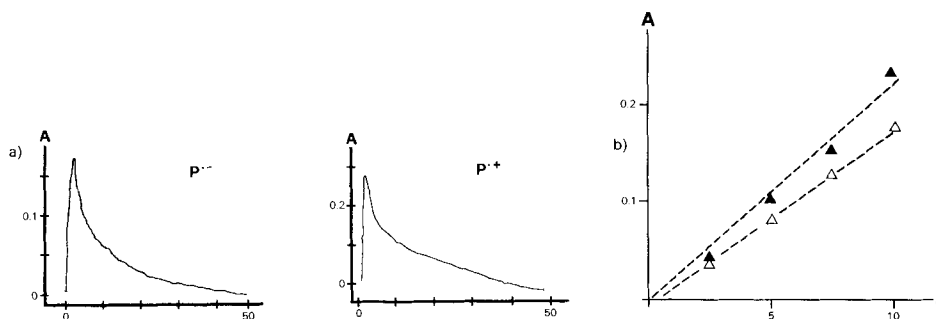


Fig. 1. a) Transient absorptions of the perylene radical cation  $P^+$  (at 540 nm) and radical anion  $P^-$  (at 580 nm) in deoxygenated MeCN (abscissa in  $t/\mu$ s, ordinate in absorbance units); b) Initial optical density of  $P^+$  ( $\blacktriangle$ ) and  $P^-$  ( $\triangle$ ) as a function of laser light intensity I (in mJ)

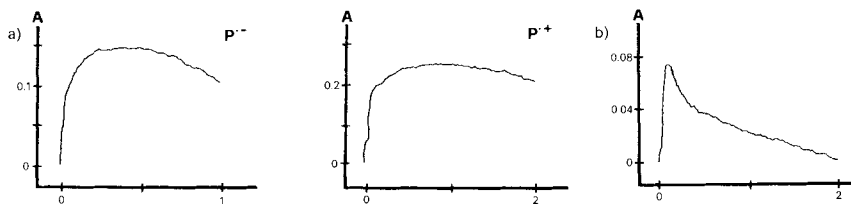


Fig. 2. a) Transient absorptions of  $P^+$  (at 540 nm) and  $P^-$  (at 580 nm) in deoxygenated MeCN at short times (abscissa in  $t/\mu$ s, ordinate in absorbance units); b) Transient absorption of  $P^+$  (at 540 nm) in air-saturated MeCN (abscissa in  $t/\mu$ s, ordinate in absorbance units)

<sup>1)</sup>  ${}^1P^{**}$  is used for P excited to an upper electronic and/or vibrational state.

The reaction  ${}^1P^* + P \rightarrow$  ions cannot account for a 400-ns risetime in the ion absorption, since the competitive deactivation of  ${}^1P^*$  by fluorescence and intersystem crossing gives a lifetime of at most 7.5 ns. With such a short lifetime, the rise in ion concentration would be practically complete (to 99.9%) within 80 ns. When the concentration of P is lowered the initial  $P^{+\cdot}$  and  $P^{-\cdot}$  absorptions decrease as shown in Fig. 3.

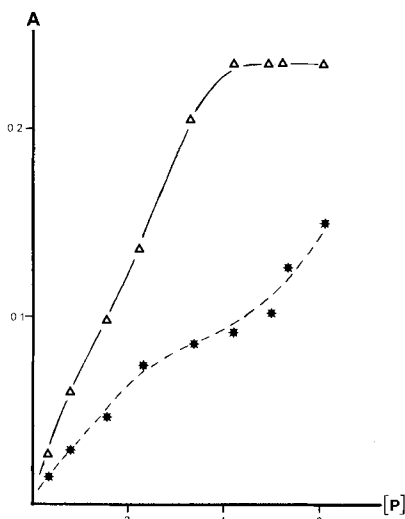


Fig. 3. Relationship between the initial optical density of  $P^{+\cdot}$  (at 540 nm;  $\Delta$ ) and  $P^{-\cdot}$  (at 580 nm; \*), and  $[P]$  ( $\times 10^{-4}$  M)

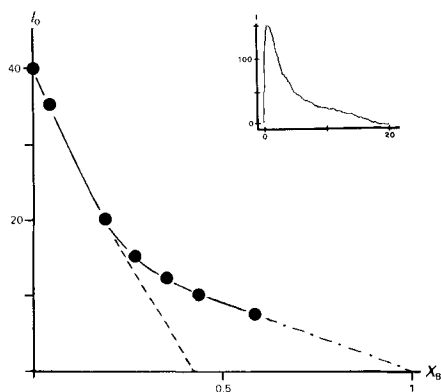


Fig. 4. Initial transient photocurrent  $I_0$  (in  $\mu$ A) as a function of benzene mole fraction ( $X_B$ ) in MeCN. Insert: kinetics of photocurrent decay (abscissa in  $t/\mu$ s, ordinate in  $\mu$ A).

The transient photocurrent in a  $2.8 \times 10^{-4}$  M deoxygenated solution of P in MeCN shows the presence of charge carriers (Fig. 4). In neat benzene solution, no transient photocurrent is observed down to  $\sim 2 \mu$ A in similar conditions, although small absorptions in the ions' wavelength region exist with lifetimes of the order of 600 ns. This raises the intriguing possibility that geminate ion pairs may be formed even in benzene but that these ions cannot separate and do not act therefore as independent charge carriers [4]. In mixtures of benzene/MeCN the  $P^{+\cdot}$  and  $P^{-\cdot}$  absorptions show quite different variations

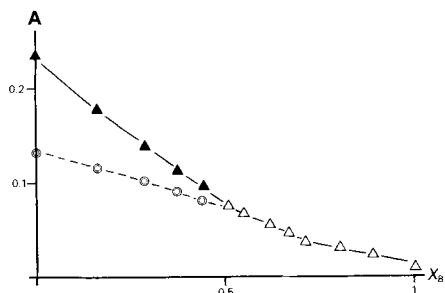


Fig. 5. Initial optical density of  $P^{+\cdot}$  (at 540 nm;  $\blacktriangle$  and  $\Delta$ ) and  $P^{-\cdot}$  (at 580 nm;  $\circ$  and  $\triangle$ ) as a function of benzene mole fraction ( $X_B$ ) in MeCN

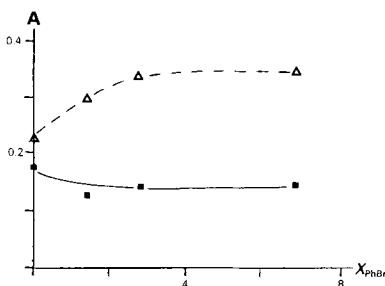
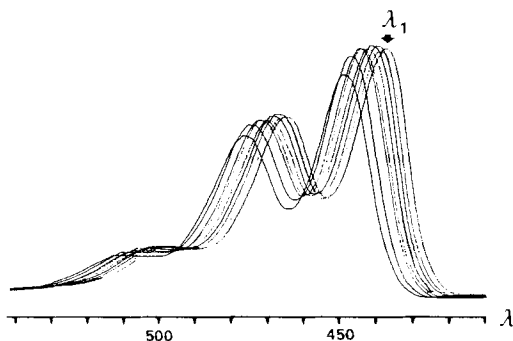


Fig. 6. Initial optical density of  $P^{+\cdot}$  (at 540 nm;  $\Delta$ ) and  $P^{-\cdot}$  (at 580 nm;  $\blacksquare$ ) as a function of PhBr mole fraction ( $\times 10^{-3}$ )

with MeCN mole fraction, as shown in *Fig. 5*. This observation as well as the effect of  $[P]$  described above suggests that two independent reaction mechanisms can form  $P^{+\cdot}$ .

When PhBr is added to a solution of P ( $2.8 \times 10^{-4}$  M) in MeCN, the absorption attributed to  $P^{+\cdot}$  increases while that due to  $P'^{-}$  remains more or less unchanged (*Fig. 6*). However, PhBr does not quench the fluorescence of P, even at very high concentrations; its only effect is to shift the fluorescence spectrum but the emission quantum yield remains unchanged (*Fig. 7*). The solvatochromic shift of the fluorescence spectrum can obviously give the appearance of a quenching when the emission intensity is monitored only at one single wavelength (e.g.  $\lambda_1$  in *Fig. 7*).



*Fig. 7.* Solvatochromic shift (in nm) of the fluorescence spectrum of P in MeCN with increasing concentration (from right to left) of PhBr. Spectrum to the right (label  $\lambda_1$ ) corresponds to  $[PhBr] = 0$ ; spectrum to the left corresponds to neat PhBr.

PhBr acts as an electron scavenger according to



The yield of free  $P^{+\cdot}$  is then increased as the recombination process



becomes less efficient.

Molecular oxygen has a 'quenching' effect rather similar to that of PhBr. It cannot, therefore, be assumed that  $O_2$  quenches excited singlet aromatics only by increasing the rate of intersystem crossing. There is clear evidence from the increase in the yield of  $P^{+\cdot}$  with increasing  $[O_2]$  that part (possibly the major part) of this quenching action results from an electron-scavenging process similar to *Eqn. 5* above.

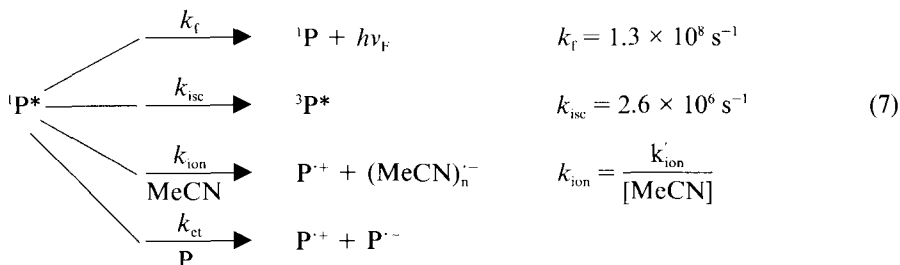
The ion yields have been calculated from the initial absorbance at the relevant wavelengths and the known extinction coefficients [5], the optical pathlengths being 5 mm (see *Experimental*). These data are listed in the *Table*. The regions of absorption of the ions  $P^{+\cdot}$  and  $P'^{-}$  correspond to those reported for these species prepared in low-temperature rigid matrices [5].

*Table.* Ion Yields from Initial Absorbance  $\Delta D_o$  at  $\lambda_{max}$  (540 nm for  $P^{+\cdot}$ , 580 nm for  $P'^{-}$ ).  $c_o$  is the initial ion concentration,  $n_{ion}$  the number of ions in the irradiated volume (0.14 ml) and  $nh\nu_{abs}$  the number of photons of laser light absorbed in the same volume.

	$\epsilon_{max}$	$\Delta D_o$	$c_o$	$n_{ion}$	$nh\nu_{abs}$	$\Phi_{ion}$
$P^{+\cdot}$	$5 \times 10^4$	0.08	$2.7 \times 10^{-6}$	$2.3 \times 10^{14}$	$9 \times 10^{15}$	$2.4 \times 10^{-2}$
$P'^{-}$	$5 \times 10^4$	0.05	$1.7 \times 10^{-6}$	$1.4 \times 10^{14}$	$9 \times 10^{15}$	$1.6 \times 10^{-2}$

Finally, it should be noted that no overall photochemical reaction has been observed for P in MeCN or MeCN/benzene mixtures; the absorption spectrum of P is unchanged after prolonged irradiation in laser-flash or steady-state conditions, to quantum yields lower than  $10^{-3}$ . On the other hand, samples containing PhBr or 1,4-Br<sub>2</sub>Ph are photo-reactive but no attempt was made at this stage to isolate and characterise the photo-products. Such photoreactivity is in keeping with the electron scavenging action of PhBr in these systems and the long-term degradation of such samples is ascribed to secondary (dark) reactions of the ionic species.

**Discussion.** – PhBr does not act as a quencher of <sup>1</sup>P\* but behaves as an electron trap through reaction with the solvated electron in MeCN. This removes the main objection against Eqn. 1, the formation of the positive and negative radical ions through charge separation in the excimer (or the encounter complex). In addition, however, there is a path of direct electron transfer from <sup>1</sup>P\* to the polar solvent MeCN; the experimental evidence presented here suggests that this is a monophotonic process and that consequently the combined deactivation pathways of <sup>1</sup>P\* are



The rate constants of these processes can be estimated as follows: from the fluorescence lifetime of 7.5 ns of <sup>1</sup>P\* and the fluorescence quantum yield of 0.98 in benzene [6], the values of  $k_f$  and  $k_{isc}$  above are obtained. The yield of P<sup>+</sup> immediately after the flash can be attributed to approximately 50% electron transfer to MeCN and 50% electron transfer to P (see Fig. 5), at a concentration [P] =  $3 \times 10^{-4}$  M. If this latter process is diffusion controlled its pseudo-first-order rate constant  $k_{ct} = k_{diff} \times [P]$  is  $5 \times 10^6 \text{ s}^{-1}$ . The observed pseudo-first-order rate constant  $k'_{ion} = k_{ion} \times [\text{MeCN}]$  must then be also  $\sim 5 \times 10^6 \text{ s}^{-1}$ , so that the second-order rate constant for direct electron transfer from <sup>1</sup>P\* to MeCN ( $\sim 19$  M) is estimated as  $k_{ion} = 3 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$  assuming that all the ions escape from the solvent cage.

The ion yields calculated from these rate constants are in broad agreement with the observed yields, bearing in mind the approximations made in the calculation.

$$\Phi(\text{P}^+) = \frac{k_{ion}[\text{MeCN}] + k_{diff}[\text{P}]}{k_f + k_{isc} + k_{ion}[\text{MeCN}] + k_{diff}[\text{P}]} \approx 5 \times 10^{-2} \quad (8)$$

$$\Phi(\text{P}^{\cdot -}) = \frac{k_{diff}[\text{P}]}{k_f + k_{isc} + k_{diff}[\text{P}]} \approx 2.5 \times 10^{-2} \quad (9)$$

It is important to note that the ion yields are quite low, of the order of a few percent. For this reason, the bimolecular mechanism of Eqn. 1 cannot simply be excluded [3] on grounds of the low [P] ( $\sim 3 \times 10^{-4}$  M) used in these experiments; similarly the low triplet

yield ( $\sim 0.02$ ) does not exclude T-T annihilation as a mechanism to form ions in equally low yields.

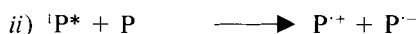
The rise in the absorption of  $P^{+\cdot}$  and  $P^{-\cdot}$  at short times after the flash in deoxygenated MeCN can be explained only by an electron-transfer path through triplet-triplet annihilation



The bimolecular ( $P^* + P \rightarrow P^{+\cdot} + P^{-\cdot}$ ) origin of the ion pairs excludes the participation of extremely short-lived upper excited species (*i.e.*  ${}^1P^{**}$  of lifetimes shorter than  $10^{-12}$  s) in these reactions. The direct photoionization of P with electron transfer to the solvent which is *competitive* with the above bimolecular process is, therefore, also unlikely to originate from such an extremely short-lived upper excited state.

The intermediacy of the excimer is hypothetical, but the process of triplet-triplet annihilation leading to repopulation of  ${}^1P^*$  is well established [7]. If this is the main deactivation pathway for  ${}^3P^*$  under our experimental conditions, then the ion yield resulting from it can be relatively high (*ca.*  $10^{-2}$ ) in spite of the low triplet yield of P.

The energy balance of the two primary processes



can be estimated from electrochemical data as follows:

The oxidation potential  $E_{\text{ox}}(P)$  in MeCN is +0.51 V *vs.* SCE [8] and the reduction potential of liquid MeCN is -3.5 V *vs.* SCE [9]. The 0-0 transition  $S_0 \rightarrow S_1$  at 445 nm places the  ${}^1P^*$  energy level at  $E^* = 3.0$  eV so that in the *Rehm-Weller* equation

$$\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E^* + C \quad (11)$$

the first three terms add up to +1.01 eV and the modified [10] [11] *Coulomb* term  $C$ , therefore, plays the determining role in the energetics. Assuming that electron transfer takes place only between contact pairs ( $P \cdot \text{MeCN}$ ) we arrive at

$$C = - \frac{e^2}{4(r_p + r_s)} = -0.53 \text{ eV} \quad (12)$$

with a net overall energy balance in *Eqn. 11* of +0.48 eV, still quite endergonic if the distance ( $r_p + r_s = 3.9 + 2.7 = 6.6$  Å) between the charges is calculated from a spherical model of P,  $r_p$  and  $r_s$  being the molecular radii of P and MeCN, respectively. P is in reality a fairly large planar structure, and it may be unrealistic to approximate it to a sphere; if the acceptor MeCN molecule must be found in the most favourable position near the centre of the ring system the effective distance is reduced to  $1.7$  Å +  $r_s$ , since the *van-der-Waals* 'thickness' of such an aromatic ring is some 3.4 Å. In this case  $C = -0.9$  eV and the energy balance comes to +0.11 eV. The rate constant  $k_{\text{ion}}$  is then in agreement with the relationship between electron-transfer rate constants and energy balance reported for an intramolecular system [12]. It is, therefore, expected that in neat MeCN solution all the solvent molecules surrounding P may not be equivalent as electron acceptors, and some experimental evidence in this direction is obtained from a further consideration of the variation in the initial photocurrent with the composition of benzene/MeCN mixture

(Fig. 4). The rapid decrease in the photocurrent at low benzene (PhH) mole fractions gives an intercept for zero photocurrent at a mole fraction  $X_{\text{PhH}} = 0.35$ , whereas it could be expected to decrease linearly to  $X_{\text{PhH}} = 1$ , if all the MeCN molecules were equally effective in acting as electron acceptors. Against this interpretation can be argued that the lower polarity of the solvent mixture would result in a faster geminate ion-pair recombination which would lower the ion yield, even if no MeCN molecules have a privileged position in the solvation shell of P. Such an interpretation of the drop in photocurrent with increasing benzene mole fraction is made doubtful by the observation that the lifetime of  $P^{+\cdot}$  (i.e. its recombination time) remains the same in the solvent mixtures even at quite low MeCN concentrations (0.5M). This can be explained, if the escaped ions are rapidly surrounded by a shell of nearly neat MeCN by the process of dielectric enrichment, so that even in mixtures of low bulk polarity the local solvent polarity in the immediate neighbourhood of  $P^{+\cdot}$  is the same as in neat MeCN [12]<sup>2</sup>).

Turning to the second electron-transfer process *ii*, the reduction potential  $E_{\text{red}}$  of P is  $-1.68$  V in DMF<sup>3</sup>) *vs.* SCE and  $C = -0.4$  eV (taking  $3.9$  Å for  $r_p$ ). The reaction is then highly exergonic,  $\Delta G_{\text{et}} = -1.2$  eV, and a rate constant of the order of  $10^{10}$  s<sup>-1</sup> is predicted from intramolecular electron-transfer data [12]. We find here that this reaction is diffusion limited so that electron-transfer takes place at every encounter of  $^1P^*$  with P.

Since photoexcited *p*-chloranil can act as an electron *acceptor* towards MeCN [13], it is interesting to consider the energy balance of the similar electron-capture process in the case of  $^1P^*$ :  $\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E^* + C = 1.78$  eV with the most favourable *Coulomb* term of  $-0.9$  eV,  $E_{\text{red}}$  being  $-1.68$  V *vs.* SCE and  $E^* = 3$  eV. Thus, electron capture from MeCN by photoexcited P is highly endergonic and is not observed.

The secondary reactions involving the  $P^{+\cdot}$ ,  $P^{\cdot-}$ , and  $(\text{MeCN})_n^{\cdot-}$  ions need to be clarified by further work. It has been shown here that PhBr acts as an electron acceptor towards  $(\text{MeCN})_n^{\cdot-}$ , and there is at first sight no reason for other aromatic molecules of suitably low reduction potential to act otherwise. However, we found no evidence for electron capture by ground state P from  $(\text{MeCN})_n^{\cdot-}$  (if the process  $P + (\text{MeCN})_n^{\cdot-} \rightarrow P^{\cdot-} + (\text{MeCN})_n$  were efficient, the initial concentrations of  $P^{+\cdot}$  and  $P^{\cdot-}$  should be the same). Since there is no overall photochemical degradation of P/MeCN solutions (in absence of PhBr),  $P^{+\cdot}$  and  $P^{\cdot-}$  apparently separate (and live for several microseconds) only to recombine to reform the ground state neutrals. This recombination process being exergonic to some  $-1.8$  eV one may well ask why the ions separate in the first place.

While no definitive answer can be given at this stage, we note that with such highly exergonic reactions one is entering into the 'inverted region' of the *Marcus* model of electron transfer where the rate constants for such processes are expected to decrease rapidly for increasingly exergonic reactions.

**Conclusions.** – The electron-transfer reactions of photoexcited P in MeCN illustrate the range of unimolecular and bimolecular processes which are in principle feasible in such a solvent. These are all monophotonic processes and the electron transfers involve thermally equilibrated electronically excited states.

<sup>2</sup>) This applies of course only to the relatively long-lived solvated ion radicals which are observed in our ns-time-scale flash-photolysis experiments, and not to very short-lived species such as geminate ion pairs. We thank the referee for pointing out this limitation.

<sup>3</sup>) This same value is used for MeCN as solvent, which is justified by the fact that the reduction potentials of pyrene, coronene, and fluoranthene are the same in both solvents within 0.05 V [8].

**Experimental.** – Perylene (*Fluka, purum*) was recrystallized twice from UV-grade EtOH, and 1,4-dibromobenzene (*Fluka, pract.*) twice from UV-grade MeOH. MeCN (*Fluka, UV-grade*) was redistilled over P<sub>2</sub>O<sub>5</sub> and PhBr (*Fluka, puriss.*) was redistilled under Ar. The laser flash photolysis apparatus was described earlier [10]. In all transient absorption measurements the ordinates are corrected absorbances.

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