A STUDY OF THE SPECTRAL AND KINETIC CHARACTERISTICS OF TRIPLET EXCIPLEXES

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Summary

Triplet states of the magnesium monopyridinate-*meso*-tetraphenyl-porphyrin complex form exciplexes with aromatic nitro compounds. The kinetic parameters of the formation, dissociation and deactivation processes of the triplet exciplexes are determined by the nature of the quencher. The kinetic constant k_1 of exciplex formation increases with increasing electron acceptor ability of the nitro compound and reaches the value characteristic of diffusion. The rate of deactivation of the majority of exciplexes does not depend on the nature of the quencher. However, it increases for exciplexes formed by the weakest electron acceptors. The data obtained suggest that the exciplex is formed by the reorganization of encounter complexes which can also deactivate. The absorption spectra of the magnesium monopyridinate-*meso*-tetraphenylporphyrin complex and exciplexes formed by the strongest quenchers are different. This suggests that there is substantial charge transfer in the exciplexes investigated.

1. Introduction

Triplet exciplexes have been observed in liquid solutions during flash photolysis studies of the quenching of triplet molecules of metalloporphyrins by electron acceptors [1 - 4]. The complicated nature of the two-stage quenching process which occurs via the formation of triplet exciplexes first becomes apparent in the shape of the kinetic curves. The kinetics of the optical density relaxation of solutions containing a porphyrin and an electron acceptor is described by a two-component curve. The products of complete electron transfer, *i.e.* ion radicals, are not usually generated in such systems. The short-lived photoproducts are quenched effectively by oxygen, azulene and other energy acceptors of the triplet porphyrin molecules. Therefore the two-component decay kinetic curve implies the formation of triplet exciplexes. The long-lived component of the curve is believed to be due to an exciplex. In many cases its spectrum differs slightly from the triplet–triplet

absorption spectra of electron donor molecules and this suggests that there is a small charge transfer between the components of such exciplexes [2, 3]. Triplet exciplexes which underwent almost complete charge transfer were reported in a later investigation [5]. Their spectra are superpositions of the spectra of the oxidized and reduced forms of the interacting molecules.

A kinetic study of the two-component curves discussed above is presented in this paper. The data obtained allowed us to examine the effect of the quencher on the transient absorption spectra and the kinetic parameters of the quenching process proceeding via the formation of a triplet exciplex.

The magnesium monopyridinate-*meso*-tetraphenylporphyrin complex (TPhPMgPy) was investigated. It was synthesized using the procedure described in ref. 6. Aromatic nitro compounds purified by distillation or recrystallization were used as quenchers. Toluene purified using conventional techniques [7] was used as the solvent. The experiments were carried out using a flash photolysis unit (about 20 μs; flash energy, about 100 J). The solutions were degassed to a residual pressure of about 10^{-3} Pa using a high vacuum system. The concentration of TPhPMgPy in the solutions was about 5×10^{-6} mol l^{-1}. The solutions were photoexcited in the long wave region where the pigments absorb using KS-14 and OS-18 glass filters (made in the U.S.S.R.).

2. Results and their analysis

The deactivation of triplet states of TPhPMgPy molecules in the degassed solutions is satisfactorily described by a first-order kinetic equation with a rate constant of about 2×10^3 s^{-1}. The addition of a nitro compound (Table 1) to the metalloporphyrin solution changes the relaxation kinetics of the optical density. In many cases two-component curves similar to those described in refs. 1 - 4 are obtained (Fig. 1). The shapes of the kinetic decay curves in Fig. 1 are strongly affected by the wavelength which indicates that the absorption spectrum of the first component differs from that of the second component. The absorption spectrum of the first component is similar to that of the TPhPMgPy triplet (Fig. 2). The equivalent absorption band in the spectrum of the second component is shifted in the short wave direction relative to the corresponding band in the TPhPMgPy triplet–triplet absorption spectrum. The spectra given in Fig. 2 show that the position of the absorption band of the kinetic curve of the second component is characteristic of the electron-accepting properties of the quencher. Thus the maximum of the second component is at 440 - 445 nm for 1,5-dinitronaphthalene, *o*-nitrophenol and dinitromesitylene, at 450 nm for *o*- and *p*-nitroaniline and at 460 nm for *p*-nitro(*N,N*-dimethyl)aniline. The data obtained for the first and second components show that the spectra of the impulse photoexcitation products of the triplet molecules and of the exciplexes are different. A more detailed discussion of the spectral evidence

TABLE 1

Kinetic parameters of the quenching process

| Nitro compound	$E_{1/2}$ [8] (V)	$\alpha \times 10^{-4}$ (s^{-1})	β (mol^{-1} s^{-1})	$\gamma \times 10^{-7}$ (s^{-2})	$\delta \times 10^{-11}$ (l mol^{-1} s^{-2})	k_4/k_1	$\lambda_{lim} \times 10^{-3}$ (s^{-1})	$k_{-1} \times 10^{-3}$ (s^{-1})
o-dinitrobenzene		2.11 ± 1.28	<1.96 × 10^9	4.78 ± 2.3	39.5 ± 0.3	<0.27	1.4 ± 0.3	<31.4
p-dinitrobenzene	−0.48	2.49 ± 0.15	(1.19 ± 0.5) × 10^9	7.25 ± 4.21	113.5 ± 37.2	<0.11	1.65 ± 0.5	21.1 ± 0.3
α-nitronaphthalene		<4.33	<5.61 × 10^8	—	—	<0.03	1.12 ± 0.24	<40.7
Trinitromesitylene		<5.58	<5.4 × 10^8	—	—	<0.04	1.56 ± 0.57	<22.9
o-nitrochlorobenzene		0.86 ± 0.33	(1.84 ± 0.24) × 10^8	<18.83	<6.06	<1.1	1.2 ± 0.36	<4.75
m-nitroaniline	−0.94	1.82 ± 0.44	(8.76 ± 4.3) × 10^7	5.9 ± 2.36	<9.96	<0.13	1.1 ± 0.33	11.6 ± 5.8
o-nitrobromobenzene		2.39 ± 0.36	(4.73 ± 1.73) × 10^7	11.3 ± 5.5	<3.38	<0.03	0.81 ± 0.24	16.9 ± 6.1
o-nitroaniline	−1.08	1.63 ± 0.31	(3.46 ± 0.9) × 10^7	4.16 ± 1.6	2.21 ± 0.63	<0.46	2.8 ± 0.84	10.2 ± 4.4
p-nitroaniline	−1.09	<0.9	(2.94 ± 0.52) × 10^7	<0.83	<2.34	<1.1	2.8 ± 0.84	<4.7
o-nitrotoluene		2.27 ± 0.73	<2.36 × 10^7	7.34 ± 3.16	<1.5	<0.3	2.9 ± 0.87	17.6 ± 8.4
p-nitro(N,N-dimethyl)aniline	−1.09	<0.75	(2.11 ± 0.36) × 10^7	<4.89	<1.02	—	4.7 ± 1.41	<5.0
3-nitro-o-xylene		1.91 ± 0.3	(9.17 ± 0.36) × 10^6	<17.12	<1.37	—	4.25 ± 1.28	12.7 ± 4.4
o-nitro(N,N-dimethyl)aniline		1.74 ± 0.33	<4.34 × 10^6	4.55 ± 1.54	<0.26	—	7.2 ± 2.16	11.9 ± 4.5
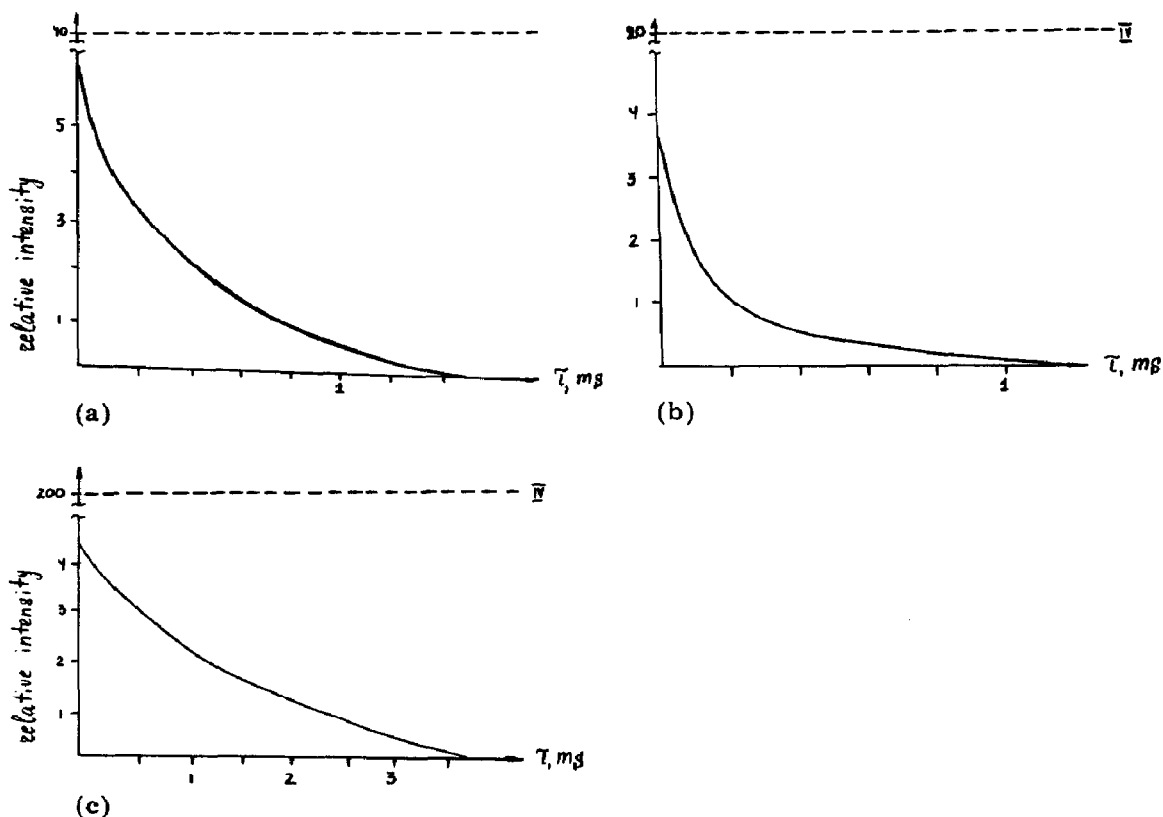
Fig. 1. The kinetics of the optical density relaxation of TPhPMgPy solutions after impulse photoexcitation (— — —, intensity of light in the cell before the flash ($\lambda = 475$ nm)): (a) in the absence of a quencher; (b) 4×10^{-5} mol o-nitrobromobenzene l^{-1}; (c) 5.9×10^{-4} mol o-nitrobromobenzene l^{-1}.

based on an analysis of the kinetic decay curves of the transient absorption is given below. The kinetic decay curves are irregularly shaped throughout the wavelength range investigated as the spectra of the first and second components overlap. It follows from an analysis of the curves that they can be linearized satisfactorily using the coordinates $X = D_1/D_0$ and $Y = D_2/D_0$ where D_0, D_1 and D_2 are the optical densities at t_0, t_1 and t_2 respectively. t_0, t_1 and t_2 are an arithmetic series in steps of Δt. The correlation factor is generally greater than 0.9. Therefore the kinetic curves can be expressed using the equation [9]

$$D = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (1)$$

The parameters of eqn. (1) were determined from an analysis of the kinetic curves performed using a BESM-6 computer (U.S.S.R.). The procedure involved a search for the zero approximation of A_1, A_2, λ_1 and λ_2 using the algorithm described in ref. 10 followed by minimization of the deviation from the sum of squares $\Sigma_i (D_i{}^c - D_i{}^e)^2$ where $D_i{}^e$ is the experimental optical density and $D_i{}^c$ is that calculated using eqn. (1). The distorted poly-
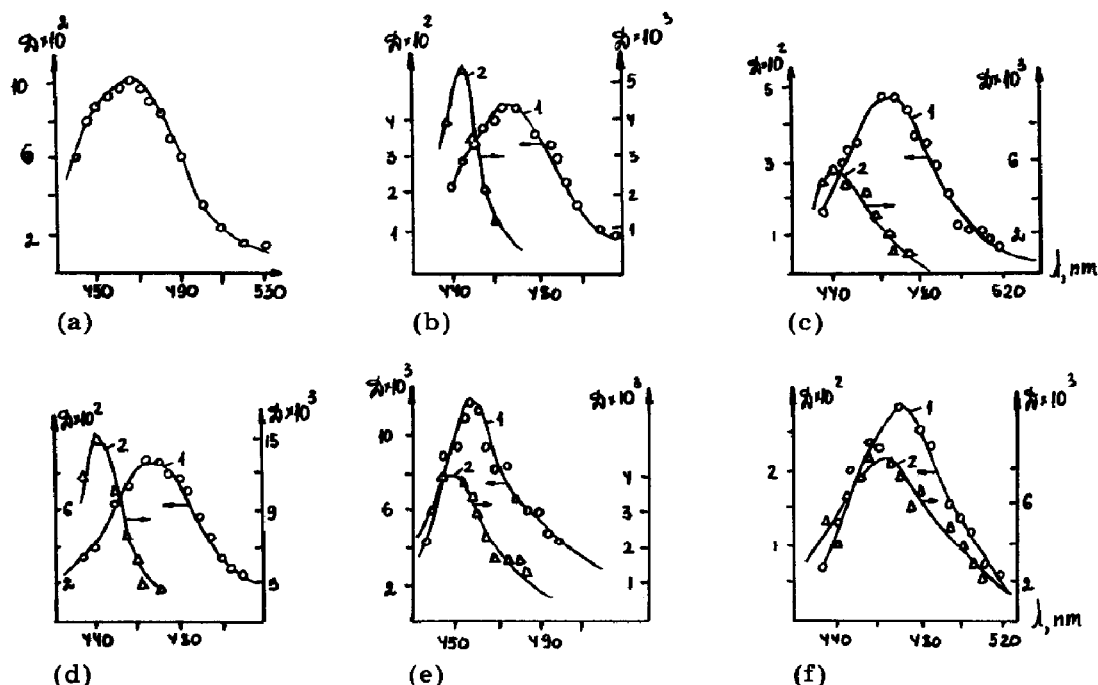
Fig. 2. Transient absorption differential spectra of toluene solutions of TPhPMgPy (curve 1, first component; curve 2, second component): (a) in the absence of a quencher; (b) 2.5×10^{-5} mol 1,5-dinitronaphthalene l^{-1}; (c) 8.4×10^{-4} mol dinitromesitylene l^{-1}; (d) 3×10^{-6} mol o-nitrophenol l^{-1}; (e) 1.9×10^{-3} mol p-nitroaniline l^{-1}; (f) 2×10^{-3} mol p-nitro(N, N-dimethyl)aniline l^{-1}.

hedron method was used for the numerical optimization of the parameters [11]. The parameters for each solution investigated were measured several times and the weighted average was determined [12].

Analysis of the curves shows (Table 2) that the characteristic time $\tau_1 = 1/\lambda_1$ for the first component decreases monotonically with increasing quencher concentration in all cases. The characteristic time $\tau_2 = 1/\lambda_2$ of the
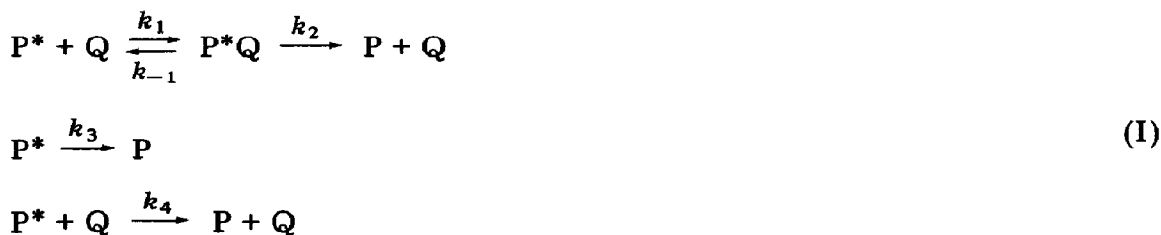
TABLE 2

The variation in λ_1 and λ_2 with the quencher concentration

o-nitrotoluene			p-nitro(N,N-dimethyl)aniline		
[Q] (mol l^{-1})	$\lambda_1 \times 10^{-4}$ (s^{-1})	$\lambda_2 \times 10^{-3}$ (s^{-1})	[Q] (mol l^{-1})	$\lambda_1 \times 10^{-4}$ (s^{-1})	$\lambda_2 \times 10^{-3}$ (s^{-1})
29.3×10^{-5}	1.45	2.7	49.1×10^{-5}	1.39	2.3
48.2×10^{-5}	1.88	2.7	75.2×10^{-5}	1.98	2.4
13.6×10^{-4}	2.97	3.6	98.3×10^{-5}	1.90	3.3
59.8×10^{-4}	—	2.9	11.8×10^{-4}	2.26	7.3
			14.7×10^{-4}	2.97	7.2

second long-lived component is unaffected by the concentration of the nitro compound in all the systems considered except the nitro(N,N-dimethyl)-anilines in which it decreases with increasing quencher concentration. It should be noted that λ_1 and λ_2 are independent of the wavelength at constant quencher concentrations.

The absorption spectra for the first and second components (Fig. 2) and the shape of the kinetic curves indicate that the quenching involves at least one long-lived intermediate. We also believe that the deactivation of the triplet molecules induced by an oxidant should be taken into account in the analysis of the kinetic data. The following scheme is therefore proposed for the quenching process:

$$P^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P^*Q \xrightarrow{k_2} P + Q$$

$$P^* \xrightarrow{k_3} P \tag{I}$$

$$P^* + Q \xrightarrow{k_4} P + Q$$

where P^* and P are TPhPMgPy molecules in the triplet and the ground electronic states respectively, Q is the quencher molecule and P^*Q is a triplet exciplex.

The conventional formal kinetic analysis of scheme (I) shows that if [Q] is much greater than [P^*] the change in the concentrations [P^*] and [P^*Q] of the triplets and exciplexes respectively is described by the equations

$$[P^*] = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \tag{2}$$

$$[P^*Q] = b_1 \exp(-\lambda_1 t) + b_2 \exp(-\lambda_2 t) \tag{3}$$

where

$$\lambda_{1,2} = \frac{B}{2} \pm \left(\frac{B^2}{4} - C \right)^{1/2}$$

$$\tag{4}$$

$$B = k_2 + k_3 + k_{-1} + (k_1 + k_4)[Q] = \alpha + \beta[Q]$$

$$C = (k_2 + k_{-1})k_3 + (k_1 k_2 + k_2 k_4 + k_{-1} k_4)[Q] = \gamma + \delta[Q]$$

The absorption spectra of the triplets and the exciplexes appear to overlap strongly and therefore the total optical density is given by

$$D = D_e + D_T = E_e[P^*Q]l + E_T[P^*]l \tag{5}$$

Substitution of eqns. (2) and (3) into eqn. (5) gives eqn. (1); eqns. (4) express the dependence of the exponents on the quencher concentration. It follows from eqns. (4) that

$$\lambda_1 + \lambda_2 = \alpha + \beta[Q] \qquad\qquad \lambda_1 \lambda_2 = \gamma + \delta[Q] \tag{6}$$

The parameters α, β, γ and δ in eqn. (6) determined by the least-squares method are given in Table 1.

Analysis of eqns. (4) shows that λ_1 increases monotonically with increasing quencher concentration whereas λ_2 tends to the limit

$$\lim_{[Q] \to \infty} \lambda_2 = \lambda_{\lim} = k_2 + k_{-1} \frac{k_4}{k_1 + k_4} \tag{7}$$

This value can also be obtained, though with less accuracy, by dividing β by δ. Table 2 shows that for most systems

$$\lambda_{\lim} < \alpha - k_3 \qquad\qquad \lambda_{\lim} < k_2 + k_{-1} \tag{8}$$

It follows from eqns. (7) and (8) that $k_4/(k_1 + k_4)$ is less than unity, $i.e.$ k_1 is greater than k_4 when the measurement errors are taken into account. The upper limit of the k_4/k_1 ratio is given by the inequality

$$\frac{k_4}{k_1 + k_4} < \frac{\lambda_{\lim} + \Delta\lambda_{\lim}}{\alpha - k_3 - \lambda_{\lim} - (\Delta\alpha + \Delta k_3 + \Delta\lambda_{\lim})} \tag{9}$$

where $\Delta\lambda_{\lim}$, $\Delta\alpha$ and Δk_3 are the measurement errors of the corresponding terms. The calculated probable upper limit of k_4/k_1 is given in Table 1.
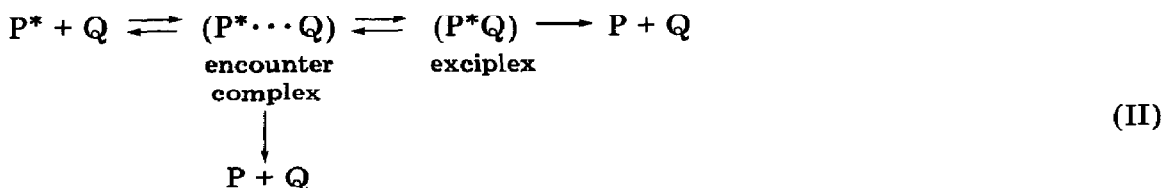
It should be noted that when TPhPMgPy triplets are quenched by p-nitroaniline and o-nitrochlorobenzene the probable upper limit of k_4/k_1 is overestimated because of the measurement errors. In these systems $\alpha - k_3 - \lambda_{\lim}$ is comparable with the errors (see eqn. (9)). However, the induced deactivation appears to proceed more slowly than the formation of the exciplex in these systems. Therefore to a first approximation we can neglect the induced deactivation whereupon $\beta \approx k_1$, $\lambda_{\lim} \approx k_2$ and $k_{-1} \approx \alpha - k_3 - \lambda_{\lim}$. The kinetic quenching parameters obtained in this way are given in Table 1.

The ratio k_4/k_1 which characterizes the deactivation of TPhPMgPy triplets by the nitro(N,N-dimethyl)anilines and 3-nitro-o-xylene appears to be less well defined. The data in Table 2 show that $\lambda_{\lim}$ and $\alpha - k_3 = k_2 + k_1$ have similar values and therefore the above procedure for determining the upper limit of k_4/k_1 cannot be used. There are a number of possible explanations for the similarity between $\lambda_{\lim}$ and $k_2 + k_{-1}$. Firstly the rate constant k_2 for the deactivation of the exciplex may exceed the corresponding values for other systems and be equal to $\lambda_{\lim}$ such that k_4 will be much less than k_1. However, the $\alpha - k_3$ values indicate that k_4 for these two systems is of the same order as for all the others. Secondly the k_2 values for the systems considered may be similar to those given in Table 1. In this case the induced deactivation should proceed more rapidly than the formation of the triplet exciplex, $i.e.$ k_4 will be greater than k_1 whereas $\lambda_{\lim} \approx k_2 + k_{-1}$. Our data are insufficient to reveal unambiguously which of these reasons explains the high $\lambda_{\lim}$ values obtained for the processes involving the nitro(N,N-dimethyl)-

anilines and 3-nitro-*o*-xylene. Nevertheless they show that the high values of λ_{lim} are evidence for an increasing role of induced deactivation in the degradation of the electron excitation energy which will be discussed in detail below.

3. Discussion of the kinetic data

The k_1 values (see Table 1) are determined by the donor–acceptor properties of the quencher: k_1 increases sharply with an increase in the electron-accepting ability of the quencher and eventually reaches the value characteristic of the diffusion region. This dependence of k_1 on the nature of the quencher indicates that the kinetics of triplet exciplex formation will be complicated. It is assumed that the process involves a preliminary complexing step:

$$P^* + Q \rightleftharpoons (P^*\cdots Q) \rightleftharpoons (P^*Q) \longrightarrow P + Q$$

encounter   exciplex
complex

$$\downarrow$$

$$P + Q$$

(II)

According to the theory of liquid phase processes the formation of the exciplexes can be considered as a reorganization of the primary encounter complex during which the reactant molecules become mutually oriented in the solvent shell corresponding to the potential energy minimum of the interaction and hence to the maximum energy stabilization of the intermediate complex. In the framework of these concepts the effect of the accepting properties of a quencher on k_1 can be interpreted as follows. On the one hand the contact time of the donor–acceptor interactions of the molecules in the encounter complex increases [13]. Therefore the probability of encounter increases and hence the rate constant of the formation of the triplet exciplex also increases. On the other hand, electron transfer may occur in the encounter complex to yield an ion–radical pair which can recombine in a non-polar solvent to give an exciplex. In this case the effect of the nature of the reactants on k_1 can be accounted for by the dependence of the electron transfer rate in the encounter complex on the donor–acceptor properties of the reactants [14]. A further more detailed study of the mechanism of the formation of exciplexes is required.

It is expected that the lifetime of triplet exciplexes will decrease with an increase in the electron-accepting properties of the quencher. However, the dependence of the triplet exciplex deactivation on the nature of the oxidant is more complicated (see Table 1). k_2 is almost independent of the electron affinity of the majority of the nitro compounds investigated here. The lifetimes of these exciplexes are similar to those of TPhPMgPy triplets in degassed solutions at room temperature. The main contribution to the deactivation of such exciplexes, as is the case for most triplet states of

aromatic molecules, appears to be quenching by residual oxygen, admixtures and solvents which masks the dependence of the quenching rate on the donor—acceptor properties of the reactants.

In the case of the exciplexes formed by the nitro(N, N-dimethyl)anilines λ_{lim} increases markedly (Table 1). As is shown above, this effect may also be due to an increase in both k_2 and k_4 compared with k_1. Both of these effects are associated with the existence of two routes for the degradation of electron excitation energy (scheme (II)). The relative contributions of these two mechanisms depend not only on the ratio k_4/k_1 but also on the stabilization energy of the exciplexes relative to the encounter complex and on the donor—acceptor properties of the interacting molecules. The lifetime of the exciplex must decrease with decreasing donor—acceptor interaction between its components at the expense of increasing the role of the deactivation mechanism involving the transfer of the exciplex to the encounter complex followed by its deactivation.

The mechanism of the induced deactivation of the excited molecules is not well understood. Nevertheless favourable conditions for intersystem crossing to the ground state can be expected to exist in the encounter complex. Repeated encounters between reactant molecules and large distances between them are known to be of great importance in the removal of spin forbiddenness in the encounter complex [13].

The data listed in Table 1 show that in general there is no obvious relation between the accepting properties of the quencher and the value of k_{-1}. It is evident that the kinetic stability of the triplet exciplex depends not only on the energy stabilization of the complex but also on the entropy factors which may partially compensate each other.

4. Transient absorption spectra

Equations (2) and (3) show that the time dependences of the concentrations of both the exciplex and the triplet are described by relationships involving two exponents. Therefore in general the spectra of the first and second components of the experimental kinetic curves are a combination of the absorption spectra of the triplets and the exciplexes. The shape of the absorption spectrum is determined by the dependence of the pre-exponential factors on the wavelength of the recording signal. A_1 and A_2 are determined from the initial conditions. The triplet exciplexes studied in this work are formed at nitro compound concentrations which have no marked quenching effects on the fluorescence of TPhPMgPy. Therefore we believe that all triplet exciplexes are formed by the interaction of triplet molecules with electron acceptors. The following initial conditions are used to calculate A_1 and A_2:

$$t = 0 \qquad [P^*Q] = 0 \qquad \frac{d[P^*Q]}{dt} = k_1[P^*]_0[Q]$$

where $[P^*]_0$ is the concentration of the TPhPMgPy triplets immediately after the flash. The application of these conditions together with eqn. (5) leads to the following equations for A_1 and A_2:

$$A_1 = \frac{k_1[P^*]_0[Q]E_e l + [P^*]_0(\lambda_1 + k_2 + k_{-1})E_T l}{\lambda_1 - \lambda_2} \tag{10}$$

$$A_2 = \frac{k_1[P^*]_0[Q]E_e l + [P^*]_0(\lambda_2 + k_2 + k_{-1})E_T l}{\lambda_2 - \lambda_1} \tag{11}$$

Equations (10) and (11) are in qualitative agreement with the experimental data (Table 3). According to these equations A_1 is generally less than A_2. It also follows that $A_1 + A_2 = [P^*]_0 E_T l$. Our data (Table 3) show that the sum $A_1 + A_2$ is approximately constant in experiments at the same excitation energy.

It follows from eqns. (10) and (11) that in general the spectra of A_1 and A_2 are a combination of those of the triplets and the exciplexes. However, their relative contributions depend on the kinetic quenching parameters. Analysis of eqns. (10) and (11) shows that for $\lambda_1 \gg \lambda_2$ the spectrum of the first component of the kinetic curve should be similar to that of the triplet–triplet absorption of TPhPMgPy. This prediction is confirmed experimentally (Fig. 2).

It follows from eqn. (10) that the contribution of the triplet molecules to the spectrum of the second component depends on the magnitude of λ_2. This is one of the reasons why the differences between the spectra of the first and second components of the kinetic curves are most marked for the process in which λ_2 is constant. In the case of the nitro(N, N-dimethyl)anilines the shape of the second component is determined by two factors: the shift in the absorption maximum of the exciplex in the long wave direction and the increase in the absorption contribution of the triplet molecules owing to the increase in λ_2 (see Table 1 and Fig. 2).

Equation (11) predicts that as the quencher concentration increases the shape of the spectrum of the second component will become more like that

TABLE 3

The variation in A_1 and A_2 and of $A_1 + A_2$ with the quencher concentration [Q]

$[Q] \times 10^5$ (mol l^{-1})	$A_1 \times 10^2$	$A_2 \times 10^2$	$(A_1 + A_2) \times 10^2$
4.0	3.30	8.03	11.33
5.0	4.23	6.33	10.56
7.9	3.87	5.50	9.37
12.1	2.90	9.22	12.12
19.6	3.43	4.57	8.00
25.0	2.05	8.40	10.45
34.0	2.47	7.30	9.77

of the triplet exciplex spectrum. However, the errors produced by a decrease in the amplitude of the transient absorption signal increase simultaneously.

Thus the transient absorption spectra give a rather distorted representation of the shape, intensity and position of the bands in the absorption spectra for triplet exciplexes. Nevertheless the spectral data indicate that there is substantial electron transfer between the components of the triplet exciplexes under study. When analysing the results given in Fig. 2 it is necessary to take into account the fact that in differential spectra the shape of the absorption band of a long-lived component is distorted by the superposition of intense "illuminance" of solutions within the Soret band region ($E_s \gg E_e$). Therefore the absorption band maximum for the exciplex is shifted in the long wave direction compared with the corresponding differential spectrum (Fig. 2). The intensive band with $\lambda_{max} = 420$ nm is known [15] to exist in the absorption spectrum of the cation radical TPhPMgPy‡. The proximity of the absorption maximum of the long-lived component for a number of systems to that of the cation radical TPhPMgPy‡ and the differences between the exciplex spectra and the triplet–triplet absorption spectra enable us to conclude that substantial charge transfer takes place in the triplet exciplexes involving TPhPMgPy. The exciplexes studied here differ in this respect from those described earlier [2]. We believe that their behaviour is due to the electron-donating abilities of TPhPMgPy.

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