

TRIPLET EXCIPLEXES — HAVE THEY BEEN DETECTED IN THE LIQUID PHASE?

I. V. RENGE

Institute of Physics, Estonian S.S.R. Academy of Sciences, Riia 142, 202400 Tartu, Estonian S.S.R. (U.S.S.R.)

V. A. KUZMIN and YU. E. BORISEVICH

Institute of Chemical Physics of the U.S.S.R. Academy of Sciences, Moscow 117334 (U.S.S.R.)

(Received February 8, 1985)

Summary

The quenching of triplet porphyrins, chlorophyll-a and anthracene by nitro compounds, quinones and organic chloro compounds and triplet phenazine by *N,N*-dimethylaniline in non-polar solvents has been reinvestigated using conventional and laser flash photolysis techniques. Contrary to earlier reports, neither kinetic nor spectral evidence has been found to corroborate the formation of triplet exciplexes in these systems.

1. Introduction

The molecular complexes of a triplet-state molecule with electron donors or acceptors are commonly called triplet exciplexes (TEs). According to refs. 1 and 2 the absorption spectra of TEs are similar either to those of the initial triplets or to those of the corresponding ion radicals. The phosphorescence emission of organic molecules and particularly TEs in solution is extremely weak and this fundamentally complicates the detection of TEs in liquid media. However, a room temperature phosphorescence-quenching study of palladium tetraphenylporphin [3] and benzil [4] has revealed weak complexing with some electron donors and acceptors. TEs should be able to transfer their excitation energy to acceptors with lower triplet energy levels such as tetracene [5] and molecular oxygen [2], although this phenomenon has not been well documented. The lifetimes of TEs are rather insensitive to the concentration of the initial quencher [1, 6, 7], which is in great excess.

The first report on TEs was published more than a decade ago [8] and a number of others then followed. Several extensive works [9, 10] have had an amazingly stimulating effect: in order to become convinced that observed signals are due to TEs some authors have only referred to refs. 9 and 10, considering a more detailed study to be superfluous [11, 12]. At this stage

of investigation, fundamental questions such as the relation between the second-order triplet quenching constants and exciplex decay constants, the reversibility of the complex formation, the location of the triplet energy level of the complex etc. have remained unresolved. For the elucidation of these problems it has turned out that a careful study of known exciplexes has been necessary. Unfortunately, we have not been able to confirm previous findings. To exclude further confusion it seems useful to report briefly on this search for long-lived TEs.

2. Experimental details

The conventional flash photolysis set-up (flash energy $E = 500$ J, time t of resolution, 5×10^{-6} s) and a nanosecond photolysis apparatus using the second harmonic of a neodymium laser ($E = 0.2$ J, $t = 2 \times 10^{-8}$ s, $\lambda = 530$ nm) have been described previously [13, 14]. Porphyrins have been synthesized and characterized using thin-layer chromatography, high pressure liquid chromatography, nuclear magnetic resonance spectroscopy and visible spectroscopy by A. F. Mironov and coworkers. Chlorophyll-a (Chl-a) was isolated from nettle leaves according to ref. 15. Other substances were vacuum sublimed, distilled in vacuum or recrystallized. The solutions were placed in a quartz vessel with a cylindrical spectroscopy cell 8 cm in length, or in a 1 cm rectangular cell for the laser set-up, and degassed to 0.1 Pa O_2 . The quenching constants k_q ($M^{-1} s^{-1}$) were obtained as the slopes of the linear plots of the first-order triplet decay constants k_1 (s^{-1}) and the quencher concentration C (M).

3. Results and discussion

Table 1 contains a comparison between our results and literature data. It includes the quenching constants k_q measured at 25 °C and decay constants of the exciplexes from the literature. The details will be discussed below.

3.1. Exciplex of zinc meso-tetraphenylporphin with *p*-benzoquinone

Shakhverdov was the first to ascribe the two-component decay of triplet zinc tetraphenylporphin (ZnTPP) in the presence of 2×10^{-5} M *p*-benzoquinone (at 450 nm) to triplet complex formation [8]. Recently Porter *et al.* found that "the exciplex decays by first-order kinetics with a rate constant of $(9 \pm 3) \times 10^3 s^{-1}$, it is deactivated rapidly by oxygen but the lifetime remains constant over a wide range of *p*-benzoquinone concentrations, which implies that complexation is restricted to the formation of a 1:1 complex" [11]. Contrary to refs. 8 and 11 we have observed strictly mono-exponential decay using purified ZnTPP (2×10^{-6} - 2×10^{-5} M) at concentrations of *p*-benzoquinone up to 1×10^{-2} M (Fig. 1). A contamination of

TABLE 1

Summary of data for systems containing TEs: quenching constants k_q measured at 25 °C, literature quenching constants k_q^{lit} mostly measured at ambient temperature, and exciplex decay constants k_1^{lit} which we have attributed to artefacts

Triplet	Quencher	Solvent	k_q ($M^{-1} s^{-1}$)	k_q^{lit} ($M^{-1} s^{-1}$)	k_1^{lit} (s^{-1})	Reference
ZnTPP	<i>p</i> -Benzoquinone	Benzene	3.4×10^9	$\sim 5 \times 10^9$	$10^3 (2 \times 10^{-5})^a$	[8]
ZnTPP	<i>p</i> -Benzoquinone	Toluene	2.3×10^9	1.3×10^9	9×10^3	[11]
ZnEtioI	<i>p</i> -NO ₂ -toluene	Benzene	3.3×10^9	3×10^9	$10^5 (10^{-4})$ and $7.5 \times 10^3 (10^{-2})$	[9, 10]
ZnEtioI	DDT ^b	Benzene	$< 1.1 \times 10^6$	8.2×10^7	—	[9, 10]
ZnEtioI	C ₂ Cl ₆	Benzene	3.8×10^4	1.4×10^8	2.5×10^4	[9, 10]
ZnEtioI	CCl ₄	Benzene	$< 1.7 \times 10^5$	3×10^7	—	[9, 10]
ZnEtioI	C ₆ Cl ₆	Benzene	$< 5 \times 10^3$	6.7×10^7	TE ₂ ^c	[9, 10]
ZnEtioI	<i>p</i> -C ₆ H ₄ Cl ₂	Benzene	$< 10^3$	4×10^7	TE ₂ ^c	[9, 10]
EtioI	NO ₂ -benzene	Benzene	1.55×10^3	5×10^5	TE ₂ ^c	[10]
Anthracene	<i>p</i> -NO ₂ -toluene	Benzene	2×10^4	4×10^5	$2.6 \times 10^4 (10^{-2})$	[9, 10]
Anthracene	CCl ₄	Benzene	$< 10^3$	1.6×10^7	—	[9, 10]
Chl-a	<i>p</i> -Benzoquinone	Toluene	3.5×10^9	5×10^9	$5 \times 10^3 (10^{-4})$	[5]
Chl-a	Substituted NO ₂ -benzenes	Toluene	—	$10^5 \cdot 10^{10}$	TE ₂ ^c	[16]
Phenazine	<i>N,N</i> -dimethylaniline	Benzene	1.7×10^6	—	—	—
Phenazine	<i>N,N</i> -dimethylaniline	<i>n</i> -Heptane	1.2×10^6	—	—	—
Phenazine	<i>N,N</i> -dimethylaniline	Toluene	—	3.5×10^6	5×10^2	[12]

^a Numerals in parentheses give the molar concentration *C* of the quencher.

^b DDT, 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane.

^c TE₂, TE with two acceptor molecules.

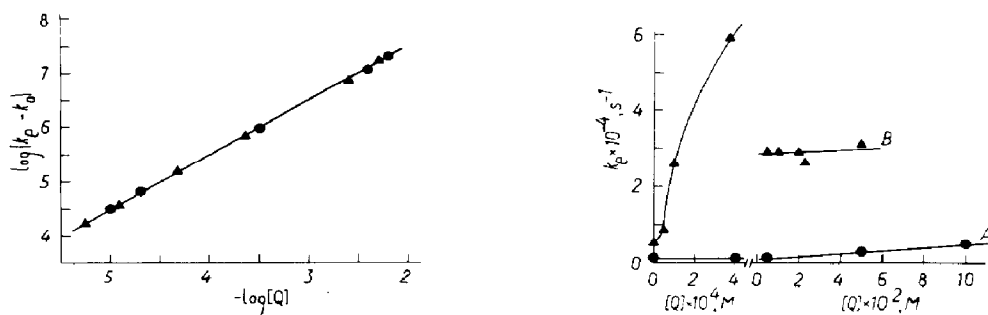


Fig. 1. Relationship between the acceptor-induced triplet-state decay constant k_e (s^{-1}) (k_0 (s^{-1}), decay constant without quencher) and the molar concentration of the quencher in benzene at 25 °C: ●, ZnEtioI triplet plus *p*-nitrotoluene; ▲, ZnTPP triplet plus *p*-benzoquinone. A logarithmic scale is used to accommodate all the data in a single plot.

Fig. 2. Plot of the triplet-transient decay constant vs. C_2Cl_6 concentration for ZnEtioI in benzene at 25 °C (curve A) and according to ref. 9 (curve B).

free-base TPP in commercial samples of ZnTPP could readily explain the non-exponentiality of flash-induced optical density decay. Because of a higher oxidation potential (TPP, 0.95 V *versus* SCE [17]; ZnTPP, 0.71 V *versus* SCE [18] (SCE, standard calomel electrode)) and a lower excitation energy (TPP, 1.4 eV; ZnTPP, 1.60 eV [11]) the triplet metal-free porphyrins are rather unreactive towards the acceptors in comparison with metalloporphyrins [19] — the constants k_q for quenching of TPP and ZnTPP by *p*-benzoquinone in benzene are $1.4 \times 10^5 M^{-1} s^{-1}$ and $3.4 \times 10^9 M^{-1} s^{-1}$ respectively. The differential spectra and the lifetimes of the triplet TPP and ZnTPP are nearly identical. Without the quencher the presence of a small amount of metal-free TPP in ZnTPP may remain undetected in flash photolysis experiments. When *p*-benzoquinone is added, only the lifetime of ZnTPP triplet will be reduced, resulting in a two-component response. The long-lived component may be erroneously ascribed to a TE, as it is quenched by O_2 .

3.2. Exciplexes of porphyrins and anthracene with nitrobenzenes and chloro-organic compounds

According to Roy *et al.* [9] and Whitten *et al.* [10] the interaction between triplet zinc etioporphyrin I (ZnEtioI), zinc octaethylporphin, etioporphyrin I (EtioI) and anthracene with electron acceptors (substituted nitrobenzenes and organic polychloro compounds) in benzene exhibited a rather complex behaviour. After the transient lifetime levelled off at moderate acceptor concentrations (Fig. 2 (curve B), Fig. 3 (curve B)) in some cases a remarkable stabilization of the species was observed at higher quencher concentrations (Fig. 3 (curve B)). These effects were rationalized in terms of the complexation of the triplet with one or two molecules of the acceptor, the ternary complexes decaying more slowly than the binary complexes.

We failed to reproduce these results. The results of this reinvestigation are shown in Figs. 1, 2 (curve A), 3 (curve A) and 4 and are summarized in

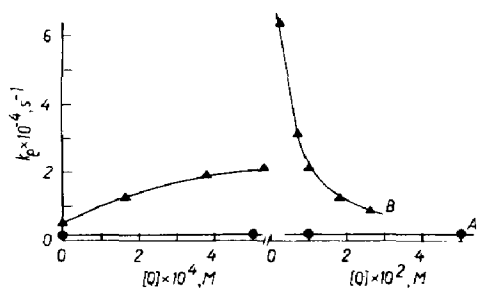


Fig. 3. Plot of the triplet-transient-decay constant vs. *p*-dichlorobenzene concentration for ZnEtioI in benzene at 25 °C (curve A) and according to ref. 9 (curve B).

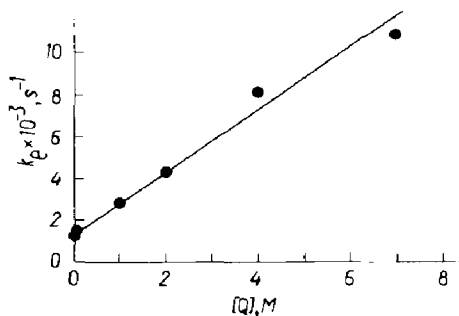


Fig. 4. Relationship between the triplet-decay constant for free-base EtioI and the concentration of nitrobenzene in benzene at 25 °C.

Table 1. The decay kinetics of triplet porphyrins and anthracene are exponential with an effective constant k_{eff} (s^{-1}). k_{eff} strictly obeys a linear relationship in the whole accessible concentration range of the quencher:

$$k_{\text{eff}} = k_0 + k_q[\text{Q}]$$

where k_0 is the triplet decay constant without quencher.

The maximum concentration of the acceptor is restricted either by the resolution time of the laser set-up (ZnEtioI plus 0.01 M *p*-nitrotoluene etc.), the solubility of the quencher ($[\text{C}_6\text{Cl}_6] = 0.2 \text{ M}$) or the drastic reduction of the triplet yield owing to the excited-singlet quenching [20] (anthracene plus 0.3 M *p*-nitrotoluene; EtioI plus 7 M nitrobenzene). The k_q values obtained in the present work are actually 2 - 4 orders of magnitude lower than those reported in refs. 9 and 10. These discrepancies can be at least partially explained by the fact that solutions of porphyrins and anthracene in the presence of organic chlorides are subject to efficient irreversible bleaching under continuous excitation (the probing beam) as well as flash excitation. The photoproducts show modified triplet-state behaviour and quenching ability.

3.3. Exciplexes of Chl-a with electron acceptors

The existence of analogous non-polar TEs of photosynthetic porphyrins with electron acceptors [5, 16] also seemed open to doubt. According to refs. 5 and 16 the transient absorption (depletion) signal from the TE of Chl-a and *p*-benzoquinone was about 100 times weaker than that from the initial triplet. To account for this, it was assumed that Chl-a is present as a mixture of two stereoisomeric forms, only one of which gives a long-lived ($3 \times 10^{-4} \text{ s}$) TE [16]. The TE could transfer its excitation energy to O_2 and tetracene though it was deactivated by neither *p*-benzoquinone [5] nor nitro compounds [16].

Indeed, we have confirmed the existence of a very low intensity "tail" in the triplet-Chl-a decay response (about 3% of the initial triplet absorption)

TABLE 2
Summary of TE decay constants k_1^{lit} and triplet quenching constants k_q^{lit} for some systems

Excited molecule	Donor or acceptor	Solvent	k_1^{lit} (s^{-1})	k_q^{lit} ($M^{-1} s^{-1}$)	Reference
Pyrene	<i>N,N</i> -diethylaniline	Toluene - (2 - 20) vol. % CH ₃ CN	2×10^7		[23]
9-Phenylacridinium cation	Biphenyl, naphthalene, 2-naphthol, phenanthrene	CH ₃ CN - 10^{-2} M HClO ₄	(1 - 4) $\times 10^4$		[2]
Benzil	Anisole	Cyclohexane	(3.5 - 7.2) $\times 10^4$	7.3×10^3	[4]
Benzil	Benzonitrile	Cyclohexane	(1.1 - 2.5) $\times 10^5$	1.1×10^4	[4]
2,6-Diphenyl-1,4-benzoquinone, duroquinone	Aromatic amines, 2-methoxynaphthalene	Various	$2 \times 10^5 - 10^8$	$10^7 - 10^{10}$	[1, 24 - 26]
Benzil	Triethylamine	CH ₃ CN - 12 vol. % H ₂ O	1.8×10^7	1.3×10^9	[27] ^a
Palladium tetraphenylporphin	<i>N,N</i> -dimethylaniline	Pyridine	$\sim 10^4$	$\sim 10^5$	[3]
PAMP	Triethanolamine	Benzene	(9 \pm 1) $\times 10^6$	1.4×10^9	[29] ^b
PAMP	Methyldiethanolamine	Cyclohexane	(9 \pm 1) $\times 10^6$	1×10^9	[29] ^b
Benzophenone	Triethylamine	CH ₃ CN	6.6×10^{10}	—	[30]
Zinc tetra- <i>tert</i> - butylphthalocyanine	<i>p</i> -Benzoquinone	Hexane, ether	(1 - 4) $\times 10^4$	3×10^7	[6] ^c
AlOH tetraphenylporphin	Quinones	Toluene	$\sim 10^4$	$10^8 - 10^9$	[7] ^c

PAMP, 1-phenyl-2-acetoxy-2-methylpropan-1-one.

^aThe interpretation of the delayed formation of reduced benzil in terms of an exciplex was later abandoned by the author himself and ascribed to the consecutive abstraction of two hydrogen atoms from (C₂H₅)₃N by triplet-state and ground-state benzil molecules giving two ketyl radicals (or radical anions) [28].

^bA TE was invoked to explain the delayed formation of radicals; see footnote a.

^cIn our opinion, the reinvestigation of these systems is also essential.

in toluene containing *p*-benzoquinone. This effect might be caused by a small amount of pheophytine-a, which could be formed when Chl-a is exposed to the air humidity and/or CO₂ [15]. Electron acceptors deactivate triplet pheophytine-a at least 10⁴ times less efficiently than Chl-a, as one could estimate [19] from the difference in electron-abstraction energies of the triplets (0.38 eV [21]).

3.4. Exciplex of phenazine with *N,N*-dimethylaniline

Recently a paper on the TEs of phenazine and benzophenazines with *N,N*-dimethylaniline in the microsecond and millisecond time scale has appeared [12]. Our experiments demonstrated that under flash excitation a solution of phenazine (5×10^{-5} M) and *N,N*-dimethylaniline in *n*-heptane and benzene indeed revealed complex changes in absorption (at 467 nm) consisting of signals from quenched triplet and products. In the presence of air (oxygen) no changes in the decay kinetics of the products were observed except for a decrease in the yield. It remains unclear why Osipov *et al.* had considered that these transient species (possibly neutral radicals [22]) should be TEs.

Notwithstanding these important findings the answer to the question posed in the title of this paper should be yes. Table 2 lists the excited-complex lifetimes and second-order quenching constants for exciplex-forming systems from the literature. Investigations in which TEs have been invoked only on the basis of negative or variable Arrhenius activation energies for the triplet quenching process [19, 31 - 33] are excluded.

Obviously, further direct information on TEs is highly desirable. It should be noted that the extensive application of nanosecond and picosecond techniques should lead to considerable advances in this area of research [29, 30, 34].

Acknowledgments

We are very grateful to Professor A. F. Mironov (Lomonosov Institute for Fine Organic Synthesis, Moscow) for preparing and purifying the porphyrins and to Dr. A. P. Darmanyan for laser measurements.

References

- 1 V. A. Kuzmin, A. P. Darmanyan and P. P. Levin, *Chem. Phys. Lett.*, **63** (1979) 509.
- 2 V. L. Ivanov, S. A. Al-Ainen and M. G. Kuzmin, *Dokl. Akad. Nauk SSSR*, **237** (1977) 1400.
- 3 J. A. Mercer-Smith, C. R. Sutcliff, R. H. Schmehl and D. G. Whitten, *J. Am. Chem. Soc.*, **101** (1979) 3995.
- 4 T.-S. Fang, R. E. Brown, C. L. Kwan and L. A. Singer, *J. Phys. Chem.*, **82** (1978) 2489.
- 5 N. E. Andreyeva and A. K. Chibisov, *Biofizika*, **21** (1976) 24.
- 6 Ye. I. Kapinus, V. P. Stary and I. I. Dilung, *Teor. Eksp. Khim.*, **17** (1981) 100.

- 7 Ye. I. Kapinus, V. P. Stary and I. I. Dilung, *Dokl. Akad. Nauk SSSR*, 261 (1982) 907.
- 8 P. A. Shakhverdov, *Opt. Spektrosk.*, 30 (1971) 81.
- 9 J. K. Roy, F. A. Carroll and D. G. Whitten, *J. Am. Chem. Soc.*, 96 (1974) 6349.
- 10 D. G. Whitten, J. K. Roy and F. A. Carroll, in M. Gordon and W. R. Ware (eds.), *The Exciplex*, Academic Press, New York, 1975, p. 247.
- 11 A. Harriman, G. Porter and V. Searle, *J. Chem. Soc., Faraday Trans. II*, 75 (1979) 1515.
- 12 V. V. Osipov, M. N. Usachova and I. I. Dilung, *Dokl. Akad. Nauk SSSR*, 254 (1980) 407.
- 13 Yu. E. Borisevich, A. S. Tatikolov and V. A. Kuzmin, *Khim. Vys. Energ.*, 12 (1978) 474.
- 14 A. P. Darmanyan and V. A. Kuzmin, *Dokl. Akad. Nauk SSSR*, 227 (1976) 1139.
- 15 W. A. Svec, in D. Dolphin (ed.), *The Porphyrins*, Vol. 5, Academic Press, New York, 1978, p. 341.
- 16 N. E. Andreyeva and A. K. Chibisov, *Teor. Eksp. Khim.*, 15 (1979) 668.
- 17 G. Brown and D. G. Whitten, *J. Am. Chem. Soc.*, 95 (1973) 5939.
- 18 A. Stanienda and G. Biebl, *Z. Phys. Chem. N. F.*, 52 (1967) 254.
- 19 I. V. Renge, V. A. Kuzmin, A. F. Mironov and Yu. E. Borisevich, *Dokl. Akad. Nauk SSSR*, 263 (1982) 143.
- 20 V. A. Kuzmin, I. V. Renge and Yu. E. Borisevich, *Chem. Phys. Lett.*, 70 (1980) 257.
- 21 G. R. Seely, *Photochem. Photobiol.*, 27 (1978) 639.
- 22 V. A. Kuzmin, I. V. Renge and Yu. E. Borisevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 2009.
- 23 I. P. Bell and M. A. J. Rodgers, *Chem. Phys. Lett.*, 44 (1976) 249.
- 24 P. P. Levin, A. M. Vinogradov, A. P. Darmanyan and V. A. Kuzmin, *Dokl. Akad. Nauk SSSR*, 254 (1980) 1158.
- 25 P. P. Levin, A. S. Tatikolov and V. A. Kuzmin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1005.
- 26 P. P. Levin, T. A. Kokrashvili, A. P. Darmanyan and V. A. Kuzmin, *Dokl. Akad. Nauk SSSR*, 262 (1982) 1180.
- 27 M. V. Encinas and J. C. Scaiano, *J. Am. Chem. Soc.*, 101 (1979) 7740.
- 28 J. C. Scaiano, *J. Phys. Chem.*, 85 (1981) 2851.
- 29 A. Salmassi, J. Eichler, C. P. Herz and W. Schnabel, *Z. Naturforsch., Teil A*, 35 (1980) 1273.
- 30 C. G. Shaefer and K. S. Peters, *J. Am. Chem. Soc.*, 102 (1980) 7567.
- 31 Ye. I. Kapinus and V. P. Stary, *Teor. Eksp. Khim.*, 17 (1981) 35.
- 32 Ye. I. Kapinus, V. P. Stary and I. I. Dilung, *Teor. Eksp. Khim.*, 16 (1980) 401.
- 33 U. Maharaj and M. A. Winnik, *J. Am. Chem. Soc.*, 103 (1981) 2328.
- 34 E. F. Hilinski, S. V. Milton and P. M. Rentzepis, *J. Am. Chem. Soc.*, 105 (1983) 5193.