

may lead to more interest in the analysis and prediction of the crystal packing of molecular crystals and it should most certainly serve as a warning to those tempted to

study the kinetics of solid-gas reactions without due regard to differences in reactivity at different crystal faces and in different directions within the crystal.

## Spectroscopic Studies of Formation and Decay of Triplet Exciplexes. Evidence for a Limited Role of Charge-Transfer Interactions in a Nonpolar Solvent<sup>1</sup>

J. K. Roy,<sup>2a</sup> Felix A. Carroll,\*<sup>2b</sup> and David G. Whitten\*<sup>2a</sup>

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received March 23, 1974

**Abstract:** Triplet states of anthracene and metalloporphyrins such as zinc etioporphyrin I in benzene solution are quenched by low concentrations of nitro aromatics and organic chloro compounds. At high quencher concentrations, new transients are observed which are exciplexes intermediate in the quenching process. Although there is some correlation of triplet quenching rates with ease of quencher reduction, the results are not consistent with a purely charge-transfer model. The exciplexes are probably best described as weak complexes of a slightly perturbed excited state similar to ground-state donor-acceptor complexes.

Interaction of electronically excited states with ground-state molecules in processes not involving electronic energy transfer has come to be recognized as a common phenomenon in photochemistry.<sup>3</sup> Among the frequently encountered consequences of such interaction are enhanced radiationless decay, chemical reaction from quencher or substrate or between them, electron transfer resulting in ion formation, and appearance of new emission. The term "exciplex" or excited-state complex, first applied by Lumry,<sup>4</sup> has been used by numerous workers to describe the intermediates involved in these diverse phenomena. Some workers have used the term exciplex to describe photochemical reactions, even in the absence of conclusive evidence that an excited-state complex is intermediate in the chemical reaction,<sup>5</sup> and many photochemists have used the term when otherwise unexplained energy-wasting processes (such as fluorescence quenching) occur, whether or not there is direct evidence for the existence of an excited-state complex. This broad usage of the term exciplex has led to the development of some controversy over exactly what an exciplex is and what factors govern true exciplex formation.

Excited-state quenching phenomena have invited a great range of descriptions. Although the observation of exciplex emission provides strong evidence for the existence of an excited complex, exciplex occurrence has been demonstrated in several cases where no emission occurs. Several workers have attempted to fit all exciplexes and excited-state quenching interactions into one theoretical framework, while others have argued for

more vague descriptions. In particular, there has been much debate about the extent of charge-transfer character in excited-state complexes. Weller<sup>6-9</sup> has pointed out that excitation of an electron from a bonding to an antibonding orbital produces a state which should have both a lower ionization potential and a greater electron affinity than the ground electronic state. Thus, an electronically excited molecule could form charge-transfer complexes in which it is the electron donor in some cases and the acceptor in others. In support of this, Weller and coworkers have found excellent correlation of exciplex energy with donor oxidation potentials and acceptor reduction potentials for the systems they have studied. Although it seems clear that formation of ions or ion pairs may be an important decay pathway for certain types of exciplexes in polar solvents, there is still considerable uncertainty over what factors govern exciplex decay in nonpolar solvents and even as to what paths for decay are available.<sup>10</sup> Hammond and coworkers<sup>11</sup> as well as Mataga<sup>12</sup> have argued that an exciplex is a new chemical species and should have a new wave function which is some combination of various excitation resonance and charge-transfer terms (eq 1).

$$\Psi_{\text{exciplex}} = \Psi_{S^*Q} \leftrightarrow \Psi_{SQ^*} \leftrightarrow \Psi_{S^+Q^-} \leftrightarrow \Psi_{S^-Q^+} \quad (1)$$

We have previously found that exciplexes formed between excited triplets of metalloporphyrins and nitroaromatics in benzene solution can be detected by flash spectroscopy.<sup>1,13</sup> Even though they do not emit, these

(6) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968), and references therein.

(7) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 267 (1968).

(8) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969).

(9) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

(10) M. Ottolenghi, *Accounts Chem. Res.*, **6**, 153 (1973).

(11) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972), and references therein.

(12) N. Mataga and O. Tanimoto, *Theor. Chim. Acta*, **15**, 111 (1969).

(13) J. K. Roy and D. G. Whitten, *J. Amer. Chem. Soc.*, **93**, 7093 (1971).

(1) A preliminary account of a portion of this work has appeared: J. K. Roy and D. G. Whitten, *J. Amer. Chem. Soc.*, **94**, 7162 (1972).

(2) (a) University of North Carolina; (b) Davidson College, Davidson, N. C. 28036.

(3) See, for example, J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, pp 301-491, and references therein; or B. Stevens, *Advan. Photochem.*, **8**, 161 (1971).

(4) (a) M. S. Walker, T. W. Bednar, and R. Lumry, *J. Chem. Phys.*, **45**, 3455 (1966); (b) *ibid.*, **47**, 1020 (1967).

(5) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **95**, 5783 (1973).

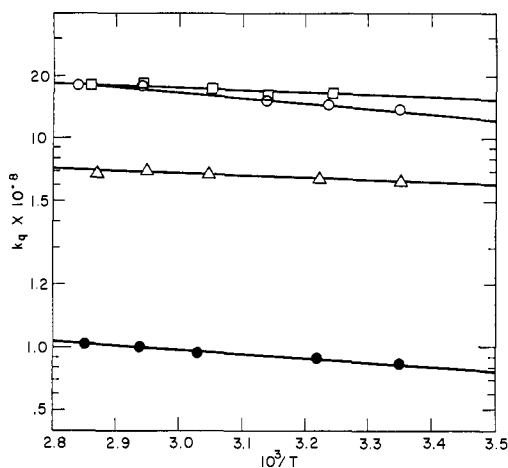


Figure 1. Arrhenius plot for quenching of zinc etioporphyrin I triplet by nitro aromatics.

relatively long-lived complexes can be quenched by other substances having low-lying excited triplets with concomitant energy transfer.<sup>1</sup> In nonpolar solvents the metalloporphyrin triplet can form both two- and three-component exciplexes having relatively long lifetimes,<sup>13</sup> while in polar media these exciplexes decay to free ions or ion pairs.<sup>1</sup> We have extended our investigations to include anthracene triplets as substrates and various chlorine-containing compounds as quenchers. The present paper focuses on the quenching process and a description of the exciplex formed in these reactions. We report results which, we believe, expand the scope of known excited-state complexes and point to a weak or limited charge-transfer interaction, such as has long been observed for ground-state systems, as a new and probably quite general reaction for excited states.

### Experimental Section

**Materials.** Porphyrins and metalloporphyrins used in this study were synthesized and purified according to published procedures,<sup>14-16</sup> and many were purified further by recrystallization from chloroform-methanol. The purity of each was estimated to be greater than 99% by uv-visible spectroscopy. Anthracene (Aldrich, 99.9%) was recrystallized from 95% aqueous ethanol and sublimed. Perylene (K&K Laboratories) was chromatographed in benzene and stored in the dark. Tetracene (K&K Laboratories) was recrystallized twice from benzene and stored in the dark. The nitrostilbenes were prepared by the Wittig reaction and purified as previously described.<sup>17</sup> The other nitro compounds and the chloro compounds were commercial products which were either distilled or recrystallized before use. Zone-refined benzene (99.9%, James Hinton, Columbia Organic Chemicals) was used as solvent for most of the work.

**Apparatus.** The flash apparatus has been described previously.<sup>18</sup> For these studies a Suntron 6C spectroscopic flashlamp (Xenon Corp., Medford, Mass.) was used; its output is estimated as ca. 50 J at 7-8 kV. RCA IP21 and IP28A photomultiplier tubes were used for some of the initial experiments. An RCA 4832 (GaAs) photomultiplier tube was subsequently employed. The latter has an essentially flat response curve throughout the 200-930-nm spectral range. A Thermistemp 63RC temperature controller with attached probe 641 (Yellow Springs Instrument Co., Yellow

Springs, Ohio) was used for variable-temperature studies. The accuracy of the system was estimated at  $\pm 0.1^\circ$ .

**Methods.** Appropriate concentrations of quencher and substrate in benzene solution were placed in a Pyrex vessel equipped with a 2.5-cm long cylindrical quartz spectroscopy cell on a side arm, a constriction, a grease trap, and a ground-glass joint. The solutions were degassed by several freeze-pump-thaw cycles and sealed under a final pressure of less than  $10^{-6}$  Torr. Porphyrin concentrations were usually  $5 \times 10^{-5}$  M and anthracene was  $\sim 10^{-4}$  M. For triplet-quenching experiments, the quencher concentration was generally  $10^{-5}$  to  $5 \times 10^{-4}$  M. For exciplex studies, considerably higher quencher concentrations were used ( $5 \times 10^{-3}$  to  $5 \times 10^{-2}$  M). The methods used to determine transient absorption spectra and decay times have been described.<sup>18</sup> The decay times reported here were determined from several experiments and are reliable to  $\pm 10\%$ .

### Results

#### Quenching of Metalloporphyrin and Anthracene Triplets.

As we have previously reported,<sup>1,13,17</sup> addition of nitro aromatics such as *p*-nitrotoluene (PNT) to benzene solutions of zinc etioporphyrin I reduces the spectroscopic lifetime of the metalloporphyrin triplet. In the present investigation we have extended our work to include several other nitro aromatics as well as a variety of organic chlorine compounds.<sup>19</sup> Values of  $k_q$  calculated from the usual Stern-Volmer relationship are listed in Table I. The chloro compounds are generally effective as quenchers of the metalloporphyrin triplet; values of  $k_q$  are in the range  $10^7$  to  $10^8$   $M^{-1}$   $sec^{-1}$ , generally about an order of magnitude smaller than those obtained for nitro aromatics. To test the possibility that these interactions are a general phenomenon of triplet-ground-state interactions, quenching of triplets of several aromatic hydrocarbons, free base etioporphyrin I, and other metalloporphyrins has been investigated. Anthracene, with a triplet energy close to that of the metalloporphyrins (42 kcal/mol<sup>21</sup>) and a slightly higher oxidation potential (1.09 V *vs.* sce in acetonitrile),<sup>22</sup> was found to exhibit behavior rather similar to the metalloporphyrins.<sup>23</sup> Anthracene triplets were found to be quenched by both organic chlorides and nitroaromatics with values of  $k_q$  in the range  $10^5$  to  $10^7$   $M^{-1}$   $sec^{-1}$  and with relative  $k_q$ 's for various quenchers roughly parallel to those observed for zinc etioporphyrin I (ZnEtioI). Values for quenching of the triplets of anthracene, zinc octaethylporphyrin (ZnOEP), and magnesium etioporphyrin I (MgEtioI) are listed in Table I.

In order to determine the thermodynamics of the quenching processes, the effect of temperature on the quenching rate constants was investigated. Values of  $k_q$  determined over a range of benzene solution temperatures from 20 to 78° showed reasonable Arrhenius correlations. Figures 1 and 2 show representative plots. Activation energies for quenching were determined from the slopes of the Arrhenius plots, and values of  $\Delta S$  (Table I) were calculated from the experimental

(19) Chloro compounds have been previously reported to quench triplets of naphthalene and other aromatic hydrocarbons.<sup>20</sup>

(20) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, *Chem. Commun.*, 745 (1968).

(21) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 86.

(22) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, p 116.

(23) Lodhi<sup>24</sup> has previously found that nitrobenzene quenches the triplet of anthracene in methylcyclohexane.

(24) S. A. K. Lodhi, *Pak. J. Sci. Ind. Res.*, **13**, 352 (1970); *Chem. Abstr.*, **75**, 27644y (1971).

(14) G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, **66**, 2517 (1962).

(15) J. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964.

(16) P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, **27**, 3342 (1962).

(17) I. G. Lopp, R. W. Hendron, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).

(18) D. G. Whitten, P. D. Wildes, and C. A. DeRosier, *J. Amer. Chem. Soc.*, **94**, 7811 (1972).

Table I. Experimental and Calculated Values for Triplet Quenching and Transient Behavior in Benzene

Substrate quencher system	$k_q \times 10^{-8}$ $M^{-1} \text{ sec}^{-1}$ <sup>a</sup>	Substrate oxidation potential, <sup>b</sup> $E_{1/2}$ (V vs. sce)	Quencher reduction potential, <sup>b</sup> $-E_{1/2}$ (V vs. sce)	Calcd energy of S+Q <sup>-</sup> state, kcal/mol <sup>c</sup>	$E_s$ , kcal/mol <sup>d</sup>	$-\Delta S$ , eu	Transient detected <sup>e</sup>
ZnEtioI-9-nitroanthracene	45	0.63					
ZnEtioI- <i>p</i> -dinitrobenzene	42	0.63	0.69 <sup>f</sup>	32.7			
ZnEtioI- <i>p</i> -nitrobenzaldehyde	34	0.63	0.89	37.4	0.35	17	
ZnEtioI- <i>cis</i> -4,4'-dinitrostilbene	31	0.63	1.00	39.8			SQ <sub>2</sub>
ZnEtioI-PNT	30	0.63	1.22	44.9	0.48	17	SQ <sub>2</sub>
ZnEtioI- <i>p</i> -chloronitrobenzene	24	0.63	1.16	43.4	0.46	17	
ZnEtioI- <i>trans</i> -1-(4-nitrophenyl)- 2-phenylpropene	20	0.63					
ZnEtioI-nitrobenzene	20	0.63	1.14	43.2	0.94	16	SQ
ZnEtioI- <i>trans</i> -4-nitrostilbene	16	0.63	1.11	42.4	1.33	17	SQ <sub>2</sub>
ZnEtioI- $\alpha$ -bromo-PNT	15						
ZnEtioI- <i>p</i> -nitroanisole	10	0.63	1.26	45.9	0.5	14	SQ <sub>2</sub>
ZnEtioI- <i>p</i> -nitroaniline	1.2	0.63	1.38	48.7	0.73	17	
ZnEtioI-hexachloroethane	1.4	0.63	0.62 <sup>g</sup>	31.1	1.2	24	SQ
ZnEtioI-DDT	0.82	0.63	0.88	37.1	1.4	23	SQ
ZnEtioI-hexachlorobenzene	0.67	0.63	1.44	50	1.5	21	SQ <sub>2</sub>
ZnEtioI- <i>p</i> -dichlorobenzene	0.4	0.63	2.05 <sup>i</sup>	64	3.2	16	SQ <sub>2</sub>
ZnEtioI-carbon tetrachloride	0.3	0.63	$\geq 2.20$	$>68$	3.3	13	
ZnOEP-PNT	19	0.53 <sup>h</sup>	1.22	42.7			
ZnOEP- <i>p</i> -chloronitrobenzene	13	0.53	1.16	41			
ZnOEP- <i>p</i> -nitroanisole	8	0.53	1.26	43.3			
ZnOEP- <i>p</i> -nitroaniline	0.6	0.53	1.38	46.3			
ZnOEP-hexachloroethane	7.1	0.53	0.62	28.8			SQ
ZnOEP-DDT	0.3	0.53	0.88	34.8	3.0	16	SQ
ZnOEP-hexachlorobenzene	0.4	0.53	1.44	47.7	10.9		
MgEtioI-nitrobenzene	18	0.46	1.14	39.2			
MgEtioI-PNT	14	0.46	1.22	41			SQ <sub>2</sub>
MgEtioI- <i>p</i> -nitroanisole	7	0.46	1.26	42			
Anthracene-PNT	0.004	1.09 <sup>j</sup>	1.22	55.6	4.7	19	SQ <sub>2</sub>
Anthracene-hexachloroethane	0.14	1.09	0.62	41.7	1.3	24	SQ <sub>2</sub>
Anthracene-DDT	0.10	1.09	0.88	47.7	3.0	24	SQ <sub>2</sub>
Anthracene-hexachlorobenzene	0.05	1.09	1.44	60.5	1.4	26	
Anthracene- <i>p</i> -dichlorobenzene	0.03	1.09	2.05	74.7	2.6	22	
Anthracene-carbon tetrachloride	0.16	1.09	$\geq 2.20$	78.1	6.7	10	

<sup>a</sup> Values at 25°. <sup>b</sup> Measured in acetonitrile or dichloromethane. We thank Mr. G. Brown for these measurements. <sup>c</sup> From eq 4; see ref 26. <sup>d</sup> Calculated from temperature dependence of  $k_q$ , corrected for change in substrate triplet lifetime with temperature. <sup>e</sup> Determined from kinetic behavior at high [quencher]; see text. <sup>f</sup> A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960). <sup>g</sup> M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949). <sup>h</sup> J. H. Fuhrhop and D. Mauzerall, *J. Amer. Chem. Soc.*, **91**, 4174 (1969). <sup>i</sup> J. W. Sease, F. G. Burton, and S. L. Nikol, *J. Amer. Chem. Soc.*, **90**, 2595 (1968). <sup>j</sup> E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963).

preexponential factors. (Values of  $k_q$  were corrected for temperature-dependent changes in the triplet lifetimes but not for changes in solvent viscosity which, over the temperature range studied, are negligible.) The activation energies for interaction of nitro aromatics with the various triplet states range from 0.5 to 4.7 kcal/mol, while those obtained for the chloro compounds are somewhat higher, in the range 1.2 to 11 kcal/mol. Entropy values for the quenching processes are all negative and are generally in the range  $-14$  to  $-26$  eu.

#### Transients Produced in the Quenching Processes.

At low quencher concentrations, an increase in quencher concentration causes only a decrease in the lifetime of the porphyrin or anthracene triplet. As was the case in our earlier studies, however, high concentrations of some quenchers led to the appearance of new transient signals. In most cases these transients had absorption spectra similar to, but not identical with, the porphyrin or anthracene triplet, but their lifetimes were quite different from those of the unquenched triplets. Figures 3 and 4 compare the spectra obtained for transients with no quencher and with high quencher concentrations for typical combinations. Figures 5 and 6 show the effect of increasing quencher concentration on tran-

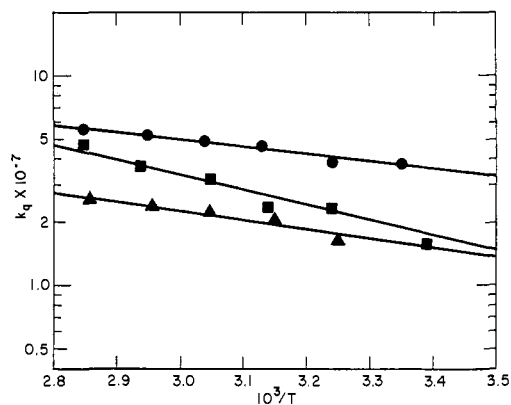


Figure 2. Arrhenius plot for quenching of zinc etioporphyrin I triplet by organic chlorine compounds.

sient lifetime in two cases which typify the two different patterns found. For zinc etioporphyrin I triplet with hexachloroethane (HCE) (Figure 5), low concentrations of HCE quenched the triplet with a rate constant  $k_q = 1.4 \times 10^8 M^{-1} \text{ sec}^{-1}$ . At higher HCE concentrations, however, the transient lifetime at 430 nm reached a limiting value of ca. 40  $\mu\text{sec}$ . The transient obtained

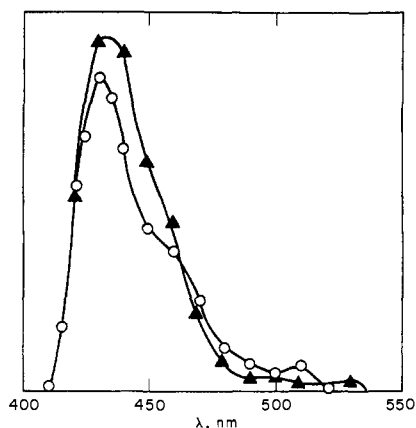


Figure 3. Transient absorption spectra for zinc etioporphyrin I in benzene (O) and for zinc etioporphyrin I-HCE (0.01 M) in benzene (▲).

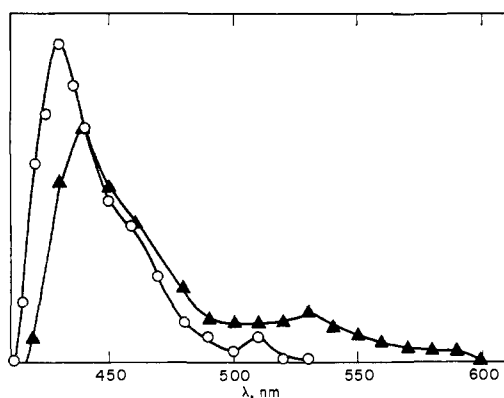


Figure 4. Transient absorption spectra for zinc etioporphyrin I in benzene (O) and for zinc etioporphyrin I-PNT (0.01 M) in benzene (▲).

at these higher concentrations had a spectrum (Figure 3) only slightly different from that of the unquenched metalloporphyrin triplet. For zinc etioporphyrin I triplets with PNT (Figure 6), low concentrations of PNT quenched the porphyrin triplet with a rate constant  $k_q = 3 \times 10^9 M^{-1} \text{sec}^{-1}$ . Here, however, at higher concentrations of PNT, an increase in transient lifetime to a maximum value of *ca.* 130  $\mu\text{sec}$  was observed. In this case the transient signal (Figure 4), although similar to the spectrum of unquenched metalloporphyrin, showed differences not evident in the transient spectrum shown in Figure 3. For the metalloporphyrin triplets, one or the other pattern was observed with all of the quenchers studied. As reported earlier, the relatively long-lived transients produced at high quencher concentrations can themselves be quenched by substances such as oxygen, azulene, tetracene, or perylene in processes that evidently involve energy transfer. For anthracene, fewer data are available, and the situation is somewhat complicated by the high quencher concentrations necessary to ensure complete quenching of the anthracene triplet (at these concentrations some singlet quenching may be interfering). However, for both PNT and HCE, long-lived transients (380 and 170  $\mu\text{sec}$ , respectively) are detected at quencher concentrations (0.01 M) high enough to reduce the anthracene triplet lifetime to negligible (below 10  $\mu\text{sec}$ ) values. In both cases, the

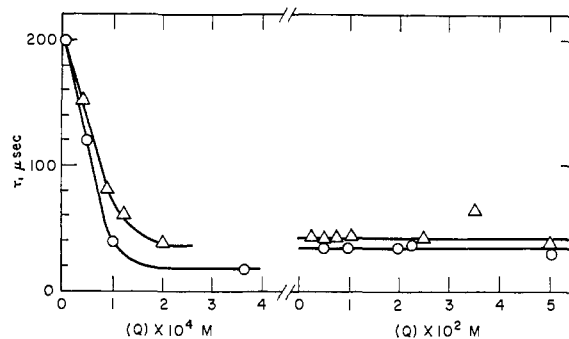


Figure 5. Plot of transient lifetime vs. quencher concentration for zinc etioporphyrin I-HCE (O) and for zinc etioporphyrin I-DDT (Δ).

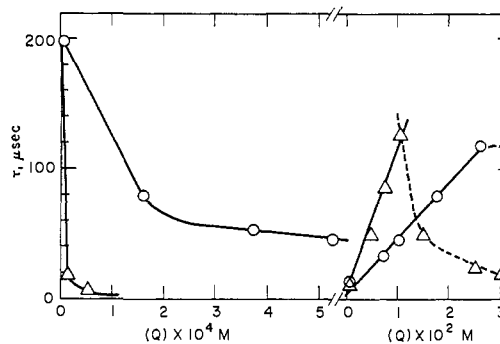


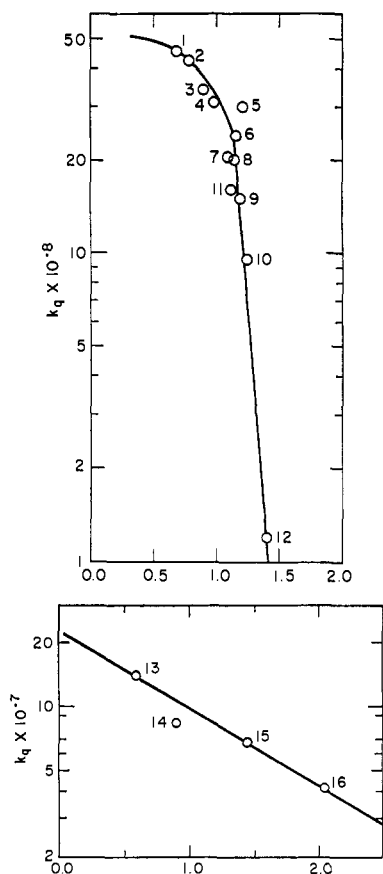
Figure 6. Plot of transient lifetime vs. quencher concentration for zinc etioporphyrin I-PNT (Δ) and for zinc etioporphyrin I-*b*-dichlorobenzene (O).

transient lifetime increases with increasing quencher concentration. Table I summarizes the transient lifetime pattern observed at high quencher concentration. A limiting transient lifetime at high quencher concentration is evidently characteristic of simple 1:1 complexes. However, those cases in which an increase in [quencher] at high quencher concentration causes a linear increase in transient lifetime are kinetically consistent with formation of a three-component exciplex in which two quencher molecules combine with a single  $A^{3*}$ .

## Discussion

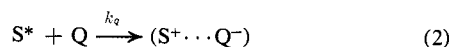
The observation that high quencher concentration leads to the appearance of transient absorption with spectral characteristics slightly different from that of the unquenched triplet suggests to us that we are observing new species formed in the quenching process. Based on the fact that these species can be quenched by substances having low-lying triplets, that they are formed in non-polar solvents, and that their spectra are different from the radical ions of the species involved (*vide infra*), we feel it is reasonable to assign the transient spectra to exciplexes intermediate in the deexcitation process.

It is perhaps useful to discuss these transients first in terms of the model developed by Weller and co-workers,<sup>6-9</sup> which suggests that exciplexes are charge-transfer complexes (radical ion pairs) which may decay to free radical ions or to ground states. Conclusions that interactions of this kind are operating usually result from correlations of Stern-Volmer quenching rate constants with electron affinity or ionization potential data. For example, if the excited state is presumed to be the



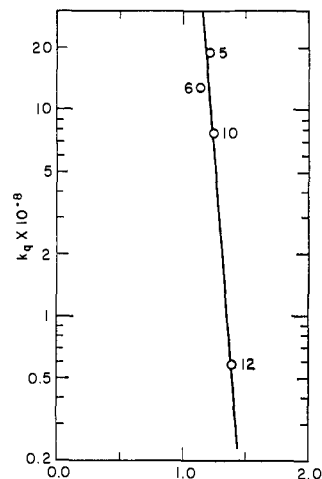
**Figure 7.** Plot of  $\log k_q$  vs. quencher reduction potential (in volts) for zinc etioporphyrin I and nitro aromatics (a) and for organic chlorine compounds (b) in benzene. Numbers refer to the following quenchers: (1) 9-nitroanthracene, (2) *p*-dinitrobenzene, (3) *p*-nitrobenzaldehyde, (4) *cis*-4,4'-dinitrostilbene, (5) PNT, (6) *p*-chloronitrobenzene, (7) *trans*-1-phenyl-2-(*p*-nitrophenyl)propene, (8) nitrobenzene, (9)  $\alpha$ -bromo-*p*-nitrotoluene, (10) *p*-nitroanisole, (11) *trans*-4-nitrostilbene, (12) *p*-nitroaniline, (13) HCE, (14) DDT, (15) hexachlorobenzene, (16) *p*-dichlorobenzene.

electron donor in forming the complex and the quencher is the electron acceptor, as shown in eq 2, it has been suggested the  $k_q$  should vary linearly with quencher reduction potential if a single  $S^*$  is quenched by a series of electron acceptors.<sup>9</sup>

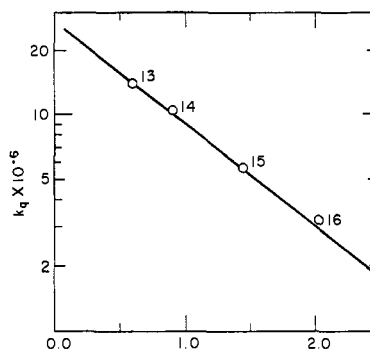


To test the applicability of such correlations in the present study, we have plotted in Figure 7 the logarithm of  $k_q$  vs. the quencher electrochemical reduction potential for quenching of the ZnEtioI triplet by a series of chloro compounds and by a series of nitro compounds. It may be seen that, while  $\log k_q$  varies linearly with  $E_{1/2}$  for nitro compounds and for the chloro compounds (with the exception of  $CCl_4$ ),<sup>25</sup> distinctly different correlations are observed. The different pattern of

(25) It should be noted that reduction of aliphatic chloro compounds is generally electrochemically irreversible. Therefore, the potentials listed in Table I and the correlations obtained in Figures 7b and 9 should be regarded with some caution. However, the fact that reasonable linear correlations are observed for plots including aliphatic as well as aromatic chloro compounds (where reduction potentials are generally reversible) suggests the potentials obtained may be fairly accurate.



**Figure 8.** Plot of  $\log k_q$  vs. quencher reduction potential for zinc octaethylporphyrin and nitro aromatics.



**Figure 9.** Plot of  $\log k_q$  vs. quencher reduction potential for anthracene and organic chlorine compounds.

reactivity between chloro compounds and nitro compounds emerged in all of the systems we investigated. Figure 8 shows a correlation of  $\log k_q$  vs. quencher  $E_{1/2}$  for nitro aromatic quenching of ZnOEP triplets. The slope of the line there is similar to that for nitro compounds in Figure 7. In Figure 9 we have plotted similar correlations for chloro compounds quenching anthracene triplets. Although the overall rate constants are much lower in these cases, the slope of the line is again almost the same as that for the chloro compounds in Figure 7. The results are reminiscent for those reported earlier for quenching of 1,4-dimethoxybenzene fluorescence by several series of compounds.<sup>26</sup> As was the case then, these results are taken to mean that charge-transfer interactions of some kind must play a role in the quenching process, but the Stern-Volmer quenching rate constant must depend on other factors in addition to simple electron-transfer parameters.

Additional and perhaps more compelling evidence that the exciplexes observed with these systems are not the charge-transfer (C-T) or ion-pair states described in eq 2 comes from an evaluation of kinetic and energetic considerations. Based on experimental results,<sup>7,27</sup> the energy of the "pure" ( $S^+ \cdots Q^-$ ) state (in benzene) described by Weller and coworkers can be expressed in

(26) F. A. Carroll, M. T. McCall, and G. S. Hammond, *J. Amer. Chem. Soc.*, **95**, 315 (1973).

(27) K. Zachariasse, Ph.D. Thesis, Amsterdam, 1972.

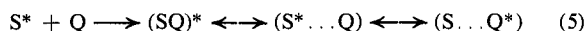
terms of measured (in acetonitrile) polarographic oxidation and reduction potentials as

$$E_{(S^+, Q^-, \text{benzene})} = E_{1/2(S/S^+)} - E_{1/2(Q^-/Q)} + 0.10 \pm 0.10 \text{ eV} \quad (3)$$

Values thus calculated for the pairs investigated are listed in Table I. In many cases the energy of this state lies well above the triplet energy of the metalloporphyrin or anthracene. However, for these cases quenching constants are only slightly below diffusion controlled and certainly not in accord with those expected on energetic grounds. For example, for zinc etioporphyrin I and PNT, the calculated heteroexcimer-state energy is 44.9 kcal/mol; an estimate of  $k_q$  based on a 3.8-kcal/mol activation energy would be *ca.*  $10^6 M^{-1} \text{ sec}^{-1}$ , yet the actual value is higher by between two and three orders of magnitude. Similarly for anthracene-PNT, the energy of the C-T state is estimated to be 55.6 kcal/mol, 13.6 kcal/mol above the anthracene triplet. An activation energy this high should lower the quenching constant ten orders of magnitude below the diffusion-controlled value, yet the actual value is  $4.4 \times 10^5 M^{-1} \text{ sec}^{-1}$ . For the chloro compounds as quenchers, calculated energies of the C-T states are too high to be consistent with the observed quenching constants in several cases. In general, the measured activation energies for triplet quenching (*vide infra*) are not at all consistent with the differences between triplet energies and the calculated C-T state energies in Table I.

The values of  $E_a$  and  $\Delta S$  reported in Table I give an additional insight into the thermodynamics of excited-state deactivation.<sup>28</sup> For the reaction of ZnEtiOI triplets with nitro aromatics, the activation energies are very small; the differences in reactivity seem to be determined more by variation of  $\Delta S$  than by variation of  $E_a$ . Furthermore, in certain cases the variation obtained in  $E_a$  among members of this series is opposite to the pattern predicted from variation in their  $E_{1/2}$  values.

In spite of the limited role of charge-transfer interactions, it seems clear that exciton resonance involving dipole-dipole terms must play an insignificant role in the quenching process. That is, the contribution of forms such as  $S \cdots Q^*$  in eq 5 probably is very small,



since there appears to be practically no correlation between  $k_q$  values and singlet or triplet energies of the compounds used as quenchers.<sup>29</sup> For the cases where the C-T state lies above the substrate triplet, the exciplex produced is probably best regarded as having its major contributions from the localized substrate triplet and the higher lying C-T state.

One of the more significant aspects of this study is the direct spectroscopic observation of the triplet exciplexes.

(28) If the experimental  $k_q$  is assumed to be a bimolecular rate constant for the reaction in eq 4, then it should be possible to study the variation of  $k_q$  with temperature to determine  $E_a$  (or  $\Delta H$ ) and  $\Delta S$  for



the reaction. For a more complex mechanism, the significance of these values might be extracted only with difficulty.

(29) On theoretical grounds, as well as from experimental evidence, the contribution of excitation resonance to the binding energy of triplet excimers or heteroexcimers is indicated to be very small.<sup>30</sup>

(30) W. Klöpffer, "Organic Molecular Photophysics," Vol. 1, J. B. Birks, Ed., Wiley, London, 1973, p 397.

This provides an opportunity to gain structural information about the exciplex that is frequently not possible in other ways, even in cases where exciplexes emit.<sup>31,32</sup> Examination of Figures 3 and 4 shows that, while not identical, the exciplex absorption spectra very closely resemble the spectra of the unquenched triplets. They do not resemble the  $S^+$  or  $Q^-$  ions whose spectra have been reported.<sup>1,35,36</sup> This suggests that in the exciplexes we observe the energy levels responsible for *ca.* 450-nm absorption are either not much altered or are all altered similarly on going from  $A^*$  to  $(AQ)^*$  (*vide infra*).

These results can be rationalized in terms of a rather nonspecific model in which the quencher molecules associate adiabatically with the excited triplet only through loose overlap of molecular orbitals with some degree of  $S^+$  to  $Q^-$  charge-transfer character. That there is some regiospecificity is indicated by the fact that  $\Delta S^*$  for the quenching is similar to the  $\Delta S$  values observed in porphyrin dimerizations.<sup>37,38</sup> The exciplex might be envisioned as being similar to the weak ground-state charge-transfer complexes that have been observed for a variety of systems, often with only small spectral perturbations. The fundamental differences between this model and that offered by Weller are that complete electron transfer almost certainly does not occur and that the orbitals involved in the charge-transfer interaction need not be the singly populated orbitals resulting from electronic excitation. Thus, the exciplex binding energy could be correlated with electron-affinity data, but the fate of the exciplex might involve paths other than ion-pair formation. The interaction would not necessarily alter the porphyrin or anthracene excited state greatly, and thus the spectral characteristics of the transient could be quite similar to those of the initial triplet.<sup>39</sup> An extreme analogy would be the acid-base reactions of excited states, such as the protonation of the  $S_1$  state of phenoxide or acridine. In nonpolar solvents then, decay of the exciplex does not normally involve ion-pair formation, and since the excitation appears to remain largely on the porphyrin (or anthracene), radi-

(31) Singlet exciplex absorption spectra have been reported in laser flash photolysis studies.<sup>10,12,33,34</sup>

(32) These results obtained in fluid medium may be compared with the behavior of phosphorescent C-T complexes in low-temperature rigid glasses. See, for example, S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 321.

(33) N. Orbach, J. Norros, and M. Ottolenghi, *J. Phys. Chem.*, **77**, 2831 (1973).

(34) R. Potashnik, C. R. Goldschmidt, M. Ottolenghi, and A. Weller, *J. Chem. Phys.*, **55**, 5344 (1971).

(35) W. I. Aalbersberg, G. J. Haijink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3049 (1959).

(36) J. H. Fuhrhop and D. Mauzerall, *J. Amer. Chem. Soc.*, **91**, 4174 (1969).

(37) J. H. Fuhrhop, P. Wasser, D. Riesner, and D. Mauzerall, *J. Amer. Chem. Soc.*, **94**, 7996 (1972).

(38) K. A. Zachariasse and D. G. Whitten, *Chem. Phys. Lett.*, **22**, 527 (1973).

(39) Since C-T interactions are certainly important, it is perhaps surprising that no "C-T" bands are detectable in the transient spectra. Possible alternative explanations to those advanced below could be that the spectra "accidentally" resemble those of the uncomplexed donor<sup>40</sup> or that the C-T bands are relatively weak or hidden in an inaccessible region of the spectra. In this regard, it is interesting to note that ground-state porphyrin-*sym*-trinitrobenzene complexes have spectra not dramatically altered from those of uncomplexed porphyrins.<sup>41</sup>

(40) J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 274, and references therein.

(41) M. Gouterman and P. E. Stevenson, *J. Chem. Phys.*, **37**, 2266 (1962).

tionless decay is probably governed largely by the radiationless decay modes available to the substrate triplet.<sup>42</sup>

As will be reported in detail elsewhere, there is a correlation between the calculated C-T-state energy and whether a two- or three-component exciplex is formed. The relatively shorter lived two-component exciplex is generally the only species detected when the calculated C-T state lies energetically close to or lower than the substrate triplet; in other cases, the three-component SQ<sub>2</sub> exciplex is formed. A reasonable explanation for this behavior is that a complex having stronger C-T contributions (the 1:1 exciplex) should have additional radiationless decay paths, while the complexes in which these contributions are less important (the 1:2 exciplexes) should have radiationless decay paths (and hence rates) similar to those of the substrate excited state.

(42) In addition to pathways available in the substrate, entirely new pathways which are inherent only to the exciplex may come into play. For example, if the quencher has heavy atom substituents, then catalysis of intersystem crossing could accompany or compete with the effects mentioned above.<sup>43-45</sup>

(43) A. R. Horrocks and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **306**, 257 (1968), and references therein, especially T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).

(44) W. H. Melhuish and W. S. Metcalf, *J. Chem. Soc.*, 480 (1958).

(45) D. O. Cowan and J. C. Koziar, *J. Amer. Chem. Soc.*, **96**, 1229 (1974).

The interactions between excited substrate and quenchers in nonpolar media where limited donor-acceptor interaction occurs, as exemplified by the present results, should probably be a fairly general phenomenon, especially for relatively long-lived triplet states. Interesting examples which may be related to the present phenomenon include the gas-phase excited-state quenching reported by Thayer and Yardley<sup>46</sup> where quenching rate correlations with electron affinity are observed, yet the quenching process almost surely does not involve electron transfer and the solution complexes between dipolar excited states and small polar molecules reported by Chandross.<sup>47</sup> It is easy to conceive of a continuum extending from specifically detectable quenching to subtle effects of the solvent on excited-state lifetimes.

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(46) C. A. Thayer and J. T. Yardley, *J. Chem. Phys.*, **57**, 3992 (1972).

(47) E. A. Chandross, "Proceedings of International Exciplex Conference," May 1974, in press.

## Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XVI. Cyclization of the 5-Hexenyl Radical<sup>1</sup>

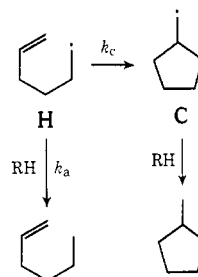
D. Lal,<sup>2</sup> D. Griller,<sup>2</sup> S. Husband,<sup>3</sup> and K. U. Ingold\*

*Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R9. Received April 16, 1974*

**Abstract:** The rate constant,  $k_c$ , for cyclization of the 5-hexenyl radical to the cyclopentylmethyl radical has been measured from  $-45$  to  $-85^\circ$  by an epr spectroscopic technique. It can be represented by  $\log(k_c/\text{sec}^{-1}) = (10.7 \pm 1.0) - (7.8 \pm 1.0)/\theta$ , where  $\theta = 2.3RT$  kcal/mol. Extrapolation of this equation yields  $k_c = 1 \times 10^5 \text{ sec}^{-1}$  at  $25^\circ$ , in excellent agreement with an earlier estimate.

Many investigators have shown that 5-hexenyl radicals, H, cyclize *irreversibly* to yield cyclopentylmethyl radicals, C.<sup>4-7</sup> The 5-hexenyl radical has become of prime importance in studies of the kinetic properties of non-resonance-stabilized, unhindered, primary alkyl radicals. It has proven particularly useful in atom transfer studies.<sup>4-6,8-10</sup> For example, in the

presence of a suitable donor, RH, both 1-hexene and methylcyclopentane may be produced. The relative



concentrations of these two hydrocarbons depend only on the concentration of RH and the rate constant ratio,  $k_a/k_c$ . Provided  $k_c$  is known, a product analysis will yield  $k_a$  for 5-hexenyl and, logically, for any other simple primary alkyl radical.

The only usable value for  $k_c$  is an estimate from these laboratories<sup>9</sup> of  $10^5 \text{ sec}^{-1}$  at  $25-40^\circ$ . This value was

(1) Issued as NRCC No. 14230. Part XV: D. Griller, G. D. Mendenhall, W. Van Hoof, and K. U. Ingold, *J. Amer. Chem. Soc.*, in press.

(2) NRCC Postdoctoral Fellow, 1973-1974.

(3) NRCC Summer Student, 1973.

(4) M. Julia, *Pure Appl. Chem.*, **15**, 167 (1967); *Accounts Chem. Res.*, **4**, 386 (1971).

(5) J. W. Wilt in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, p 333.

(6) K. U. Ingold in ref 5, p 37.

(7) Some cyclohexyl radicals are also formed at elevated temperatures.<sup>4,5</sup>

(8) C. Walling, J. H. Cooley, A. A. Ponares, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966).

(9) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

(10) C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, **94**, 6059 (1972).