PHOTO-INDUCED ELECTRON TRANSFER REACTIONS - PITFALLS AND OPPORTUNITIES

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Abstract - Benzenoid-amine systems exhibit singlet-singlet energy transfer
and exciplex formation. Factors which affect the relative importance of
these two processes are discussed. Ternary complexes can be formed between
aryl groups and two tertiary amino-groups. Such complex formation leads to
enhancement of non-radiative decay and strongly influences the efficiency
of intersystem crossing to give the aromatic hydrocarbon triplet. The part
played by conformational factors in the chemistry of electron transfer
reactions is discussed. Solvent isotope effects have been found for some
exciplex forming systems and are explained. Some aspects of the inter-
mediacy of electron transfer processes upon photo-oxygenation reactions are
discussed.

INTRODUCTION

There appear to have been several phases in the development of mechanistic aspects of photo-
chemistry. In the earliest period, absorption of a photon was considered as giving rise to
either radicals or a concerted reaction. With the increasing availability of emission
spectrometers and the development of the technique of flash photolysis, the role of the trip-
let began to dominate current thinking. This led to a search for a means to distinguish
between reactions involving excited triplets and singlets. The participation of excited
singlet states was found to be more prevalent than expected. It was during this phase that
the contribution of electron transfer processes gradually became appreciated. This was due,
in particular, to the pioneering work of Weller (Ref. 1). Interestingly the participation of
excited singlet states in electron transfer processes appeared to be more common than that of
triplet states. The balance has now been redressed and electron transfer reactions of trip-
let carbonyl compounds (Ref. 2), aromatic hydrocarbons (Ref. 3) and porphyrins (Ref. 4) etc.
have been identified.

The participation of electron transfer processes poses a complex problem. It is recognised
that such processes may involve the formation of an encounter complex, a relaxed exciplex
and radical ions (Ref. 5). Thus, three species present themselves as candidates for product
precursors. In addition, if these three species are derived from an excited singlet state,
the electron transfer process can produce triplets (Ref. 5) which in turn can act as precur-
sors for products. Examples of this type of reaction have been described (Ref. 6). Other
excited species which can act as progenitors for products include excited triplet complexes
and termolecular complexes (Ref. 7). Identifying which of these species is responsible for
product formation and how the various species are inter-related presents a challenge as well
as some inevitable pitfalls. Often it is very difficult to obtain clear-cut evidence for the
participation of a particular species and consequently negative evidence is often used to
deduce a mechanism. It is very tempting, when presented with a reaction which does not
appear to be feasible on the basis of energetics to say that it occurs via an electron trans-
fer process. Some examples of this type of problem are presented in the text.

COMPETITION BETWEEN ENERGY TRANSFER AND ELECTRON TRANSFER

The rules governing energy transfer are well described in many standard texts (Ref. 8). The
energetics of electron transfer processes have been detailed by Rehm and Weller (Ref. 9).

$$\Delta G^{\circ} = E_{OX} - E_{RED} - \frac{e^2}{\varepsilon'a} - \Delta E_{oo} \qquad \text{eq. 1}$$

where E_{OX} and E_{RED} are the oxidation potential of the donor and the reduction potential of
the acceptor respectively, $e^2/\varepsilon'a$ is the Coulombic interaction energy between the two
radical ions at the encounter distance 'a' in a solvent of dielectric constant ε' and

ΔE_{oo} is the electronic excitation energy of the fluorescer. One can therefore, from known data, determine whether a process will occur via an energy or electron transfer process. The reaction of 4-methyl acetophenone with N,N-dimethyl-p-toluidine was shown, in a recent elegant study (Ref. 10), to involve both energy and electron transfer processes.

Recently we have been examining some systems in which groups capable of undergoing electron transfer processes are separated by a rigid spacer (Ref. 11). The spacer used was the bicyclo-[2,2,2]-octane skeleton. This particular system has been used as a spacer in an earlier study, by Zimmerman (Ref. 12), on energy transfer. In the case of 1 it was found that excitation did not lead to exciplex emission whereas for 2 this was the case. It appears that for exciplex emission to be observed the donor and acceptor groups have to be

Ph—⬡—NMe₂   Ph(CH₂)₄NEt₂

_1_   _2_
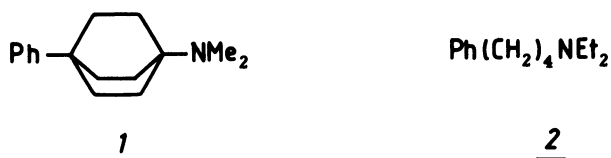
able to come relatively close to each other. The room temperature emission spectrum of 1 in cyclohexane is quite informative. The shape of the emission spectrum and wavelengths of maximal emission indicate that the emitting species resembles trimethylamine rather than the parent hydrocarbon 3, suggesting that energy transfer from the phenyl group to the amine is

Ph—⬡—H

_3_
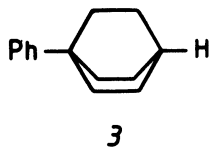
occurring. The emission spectrum of 4 in cyclohexane shows mainly fluorescence from the phenyl group. This is not surprising since, in cyclohexane the emissive state of N-methyl piperidine is very similar to that of benzene. However, if a more polar solvent is used,

Ph—⬡—N⬡

_4_
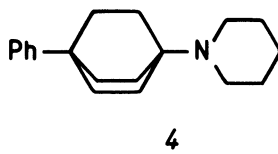
the emission of the amine moves to lower energy (Ref. 13) and the emission spectrum of 4 is composed mainly of fluorescence from the amine. Since dilute solutions (1 x 10⁻³M) were employed in the studies and the amine absorbs <10% of the incident light, it seems that energy transfer from the aryl to the amine group is occurring and that the process is intramolecular. Stress has been laid upon the fact that energy transfer is observed when the *emissive* state of the amine lies at lower energy than that of the excited singlet state of the aryl group. The emissive state of the amine is not the Franck Condon state (Ref. 14) and therefore the energy transfer process may be described as a non vertical process. It is a well known fact that many amines undergo rapid inversion at nitrogen and it is therefore conceivable that the amine will pass through its planar conformation during the lifetime of the excited aryl group and energy transfer could occur under these circumstances. There is also the possibility that the so carefully constructed bicyclo-[2,2,2]-octane framework is not insulating and that weak coupling occurs through the system via the σ-bonded framework as is shown in Fig. 1. Our lack of understanding of Rydberg states prevents us from ascertaining whether in 1 and 4 there is any significant through space interaction.

We (Ref. 15) and others (Ref. 16) have demonstrated that singlet-singlet energy transfer from benzene to many tertiary amines can be observed. Figure 2 illustrates the results obtained for the benzene-N-methylpyrrolidine system in cyclohexane. At high amine concentrations the structureless fluorescence band becomes slightly red-shifted suggesting that under these conditions other processes, e.g. exciplex formation, may be beginning to play a part. The

FIG.1   Coupling of the Aryl Group with the Amine
         via the Bicyclo [2,2,2] octane framework.

lack of observable exciplex fluorescence is at variance with the results obtained by Leismann and Mattay (Ref. 17) who found that benzene in cyclohexane solution containing triethylamine exhibited exciplex fluorescence. We (Ref. 15) subsequently showed that if high benzene
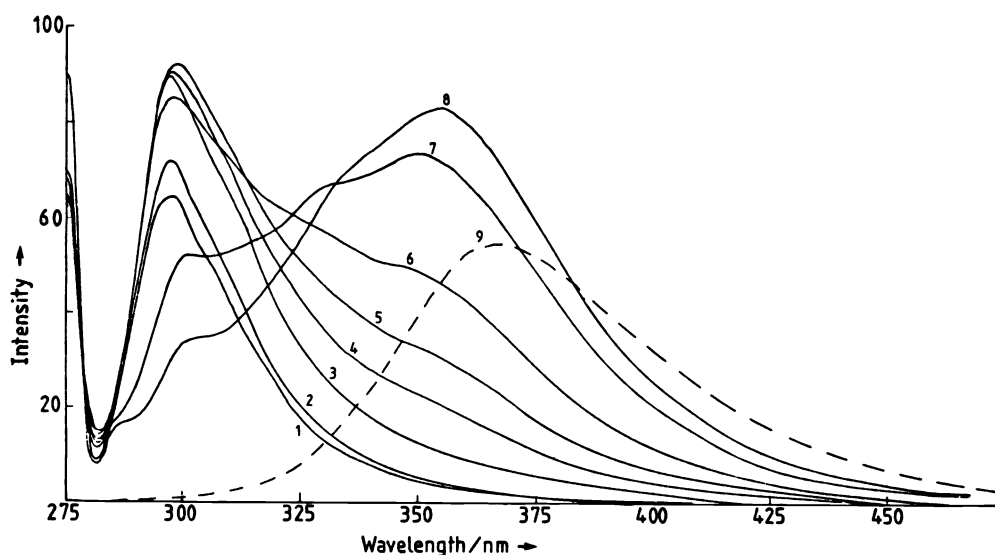

Fig. 2. Fluorescence spectra of cyclohexane solutions of N-methyl-pyrrolidine (OD = 0.1 at 275nm) containing varying amounts of benzene (λ_{exc} = 275nm). (1) 0.0M; (2) 1.88×10^{-2}M; (3) 1.88×10^{-1}M; (4) 3.75×10^{-1}M; (5) 4.63×10^{-1}M; (6) 9.4×10^{-1}M; (7) 1.50M; (8) 2.81M; (9) N-methylpyrrolidine in pure benzene (OD = 0.52 at 280nm).

concentrations are employed exciplex fluorescence is observed in preference to amine fluorescence. That exciplex formation only manifests itself when high benzene concentrations are used suggests that the benzene is not solely acting as a partner in the electron transfer process but is also acting as a solvent. Since benzene is relatively polar when compared with cyclohexane, an exciplex in an environment of benzene molecules will be of lower energy than one surrounded by cyclohexane molecules (Ref. 18). It appears therefore that in the intermolecular systems the benzene and the amine form an encounter complex which in non polar solvents gives rise to energy transfer but if the complex becomes solvated by polar molecules it will relax to give the now more energetically favourable exciplex (Fig. 3).

Another interesting feature of the benzene-amine systems relates to the fact that compounds such as 5 exhibit, in cyclohexane solution, intramolecular exciplex fluorescence to the closely related benzene — N-methylpyrrolidine system, energy transfer is observed. Presumably the oxidation potential of the amino group in 5 is similar to that of N-methyl-pyrrolidine and the reduction potential of the phenyl group is similar to that for benzene and therefore the redox parameters for 5 should be close to those for the intermolecular system.   The main difference between the inter- and intramolecular systems lies in the
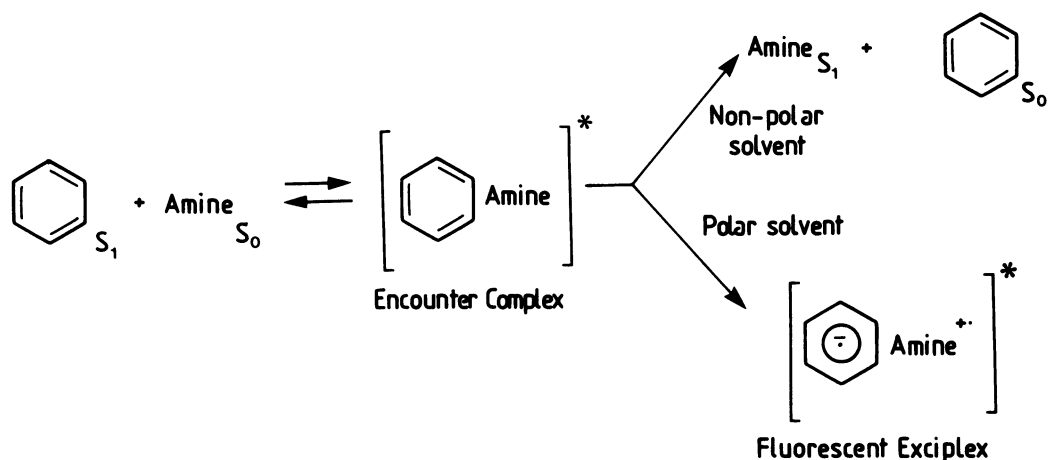
Amine S_1 + S_0

Non-polar
solvent

+ Amine

S_1 S_0

Encounter Complex

Polar solvent

Amine

Amine $+\cdot$

Fluorescent Exciplex

FIG.3   Effect of Solvent polarity upon Decay of the
         Encounter complex.

entropy factor since in **5** little re-organisation is required to attain the conformation of
the exciplex, when compared with the intermolecular system.   The entropy term can be

$$PhCH_2CH_2N$$

5
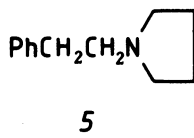
included in an equation (eq. 2) describing the energetics of exciplex formation (Ref. 19).
We believe that it is the contribution from this entropy term which lowers the energy of the
intramolecular complex relative to that of the intermolecular complex.

$$\Delta G_c = \Delta E_{oo} + E(D/D^+) - E(A^-/A) - T\Delta S_c + C \qquad \text{eq. 2}$$

(ΔG_c = free energy change for exciplex formation, ΔE_{oo} = energy of the zero-zero transition
of the hydrocarbon, $E(D/D^+)$ and $(E(A^-/A)$ are the appropriate redox potentials, ΔS_c = entropy
change and C is the free energy gained when the radical ions are brought to encounter
distance).

We have also found that energy and electron transfer are in competition in an arylcarboxylate-
amine system (Ref. 20) and in a totally different system (Ref. 21). By use of the technique
of nanosecond laser flash photolysis we (Ref. 21) and others (Ref. 22) have shown that trip-
let pyruvic acid and methyl pyruvate are deactivated by naphthalene to give triplet naphtha-
lene. The triplet naphthalene was found to have a very short lifetime and this was shown to
be due to the pyruvate quenching the triplet naphthalene (Ref. 22).   Examination of the
decay of triplet naphthalene showed that it was attended by the growth of transients which
could be ascribed to the naphthalene radical cation and the pyruvate radical anion.   Thus
energy transfer has, even if not *in toto*, preceeded the electron transfer process and this
result is reminiscent of one described earlier (Ref. 10).

EXCITED COMPLEXES CONTAINING THREE INTERACTING GROUPS

Knibbe and Weller (Ref. 23) found that the use of high amine concentrations to quench aro -
matic hydrocarbon fluorescence produced exciplex fluorescence which was red-shifted compared

with that obtained when low amine concentrations are used. They suggested that at high
amine concentrations, complexes are produced in which the aromatic hydrocarbon interacts with
two amine molecules. Subsequently the photophysics of a number of systems involving ter-
molecular complexes and related species have been examined e.g. naphthalene/1,4-dicyano-
benzene (Ref. 24), 1,3-di(1-naphthyl)propane/1,4-dicyanobenzene (Ref. 25). The study of
appropriately substituted cyclophanes has contributed enormously to our understanding of
these systems (Ref. 26). The intermediacy of termolecular and related excited complexes in
chemical reactions has also been proposed e.g. for the dimerisation of anthracene in the
presence of N,N-dimethylaniline (Ref. 27). The formation of termolecular complexes has been
put to good use by Caldwell (Ref. 28) who has developed a diagnostic test for the inter-
mediacy of exciplexes in chemical reactions.

We have found (Ref. 29) that α,ω-diaminoalkanes quench the fluorescence of aromatic hydro-
carbons and that the efficiency of this process is dependent upon the structure of the
terminal amine and the length and type of the chain linking the amino groups. The quenching
of naphthalene fluorescence by N,N,N',N'-tetraethyldiaminoalkanes in cyclohexane solution
results in exciplex fluorescence. For the diaminoethane and propane this emission is
slightly red shifted when compared with that produced by the longer chain diamines. This
suggests that the diaminoethane and propane can form complexes in which both amino groups
interact with the excited aromatic hydrocarbon. The positive evidence came from a study
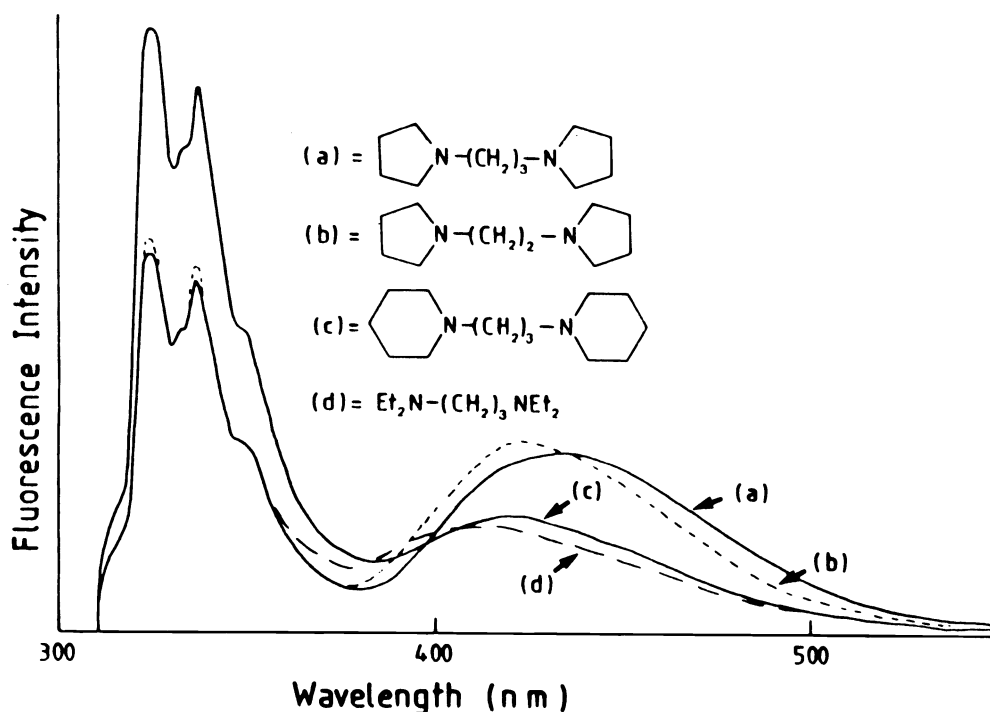employing α,ω-dipyrrolidinoalkanes and some representative spectra are shown in Fig. 4.

Fig. 4. Quenching of the fluorescence of naphthalene in degassed cyclo-
hexane solution by α,ω-diaminoalkanes.

Another notable feature of the quenching by diaminoethanes and propanes is that the exciplex
fluorescence is very weak. This can be assessed by reference to Table 1 where I_E/I_M and
I_E^∞/I_M^0 values are given. It would seem that where complex formation involving the inter-
action of three groups can take place, either new non-radiative pathways are opened up, or
the existing ones increase in efficiency.

For the diamines having > 6 methylene groups interposed between the nitrogen atoms, exciplex
fluorescence is relatively efficient. Inspection of the I_E/I_M values in Table 1 shows that
for a particular amine concentration, the diamines having n = 8 give more exciplex fluores-
cence than their corresponding mono-amines. This finding has been used to observe exciplexes
formed between a number of polycyclic aromatic hydrocarbons e.g. pyrene and anthracene, and
compounds containing the pyrrolidino and piperidino groups (Ref. 29). From the rate
constants (Tables 1 and 2) it can be seen that the diaminooctanes are far more efficient
quenchers than the related N-methyl compounds and this cannot be accounted for purely on

TABLE 1.   Quenching of naphthalene fluorescence by α,ω-diaminoalkanes and related compounds in degassed cyclohexane solution at 20°C.

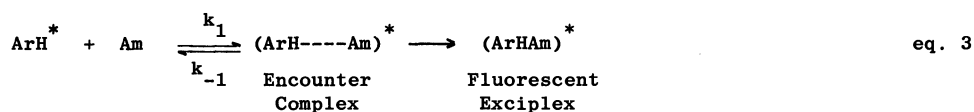| Amine	n	Quenching Rate Constant ($\ell.mol.^{-1} s^{-1}$)	I_E/I_M [a]	I_E^{∞}/I_M^{o}
Me Pyr		3.2×10^9	0.82	0.16
Pyr(CH_2)$_n$Pyr	2	5.9×10^9	0.5	0.05
	3	5.7×10^9	0.48	0.05
	8	6.0×10^9	1.2	0.12
Me Pip		0.3×10^9	0.06	0.11
Pip(CH_2)$_n$Pip	3	3.5×10^9	0.2	0.035
	8	2.1×10^9	0.4	0.12

Pyr - Pyrrolidino.   Pip - Piperidino.

a   Exciplex/monomer fluorescence intensity ratio for an amine concentration of 0.15M.

TABLE 2   Rate constants for the quenching of pyrene fluorescence by diamines in degassed cyclohexane at 20°C.

Amine	n	Quenching Rate Constant ($\ell.mol.^{-1} s^{-1}$)
Me Pyr		0.074×10^9
Pyr(CH_2)$_n$Pyr	2	2.75×10^9
	3	2.75×10^9
	8	0.78×10^9
Me Pip		0.0004×10^9
Pip(CH_2)$_n$Pip	3	0.35×10^9
	8	0.03×10^9

statistical grounds. We propose that the efficiency is due to the quenchers operating via a multi-collisional process. This process may be understood by reference to Equation 3. The overall quenching efficiency of the amine is crucially dependent upon the efficiency of
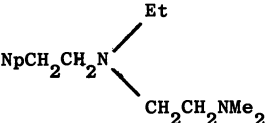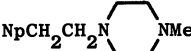
$$ArH^* + Am \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (ArH----Am)^* \longrightarrow (ArHAm)^* \qquad \text{eq. 3}$$

$$\text{Encounter Complex} \qquad \text{Fluorescent Exciplex}$$

formation (rate constant k_1) and reversal (rate constant k_{-1}) of encounter complex formation and upon the efficiency with which this complex decays to an emissive complex and radical ions etc.   For diamines in which there is the possibility of only one amino group interacting with the excited hydrocarbon in the encounter complex, the dissociation via the reaction having rate constant k_{-1} will generate the excited hydrocarbon in the vicinity of a

second amino group with which it can react and so reform the encounter complex, i.e. the presence of the second amino group increases the probability of fluorescent exciplex formation by creating an artificially high local concentration of the amine. We have termed this process multi-collisional quenching.

The formation of excited complexes involving the simultaneous interaction of three groups has been further pursued by examining purely intramolecular systems and the results are shown in Table 3. The behaviour of the compounds shown in Table 3 is in marked contrast to that

TABLE 3.   Wavelengths of exciplex fluorescence (λ nm), quantum yields of exciplex fluorescence (ϕ_F) and triplet formation (ϕ_T) for systems exhibiting ternary complex formation.

Compound	Cyclohexane			Acetonitrile		
	λ	ϕ_F	ϕ_T	λ	ϕ_F	ϕ_T
NpCH$_2$CH$_2$N（Et / CH$_2$CH$_2$NMe$_2$）	386	0.128	0.25	a	a	0.018
NpCH$_2$CH$_2$N⟨ring⟩NMe	395	0.052	0.43	a	a	0.009
NpCH$_2$CH$_2$N⟨ring⟩NCH$_2$CH$_2$N⟨ring⟩	405	0.043	0.41	a	a	0.012

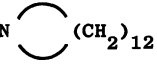Np = 1-Naphthyl.   a = no exciplex emission observable.

shown by closely related compounds such as **6** (Ref. 30) in that quantum yields of exciplex fluorescence are very low even though quenching of naphthalene fluorescence is efficient

CH$_2$CH$_2$NEt$_2$

6
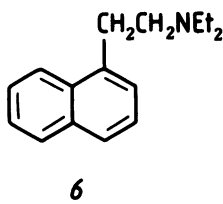
and the emission, when it can be observed, is to the red of that expected to be shown by the interaction of the aryl group with the nearest nitrogen atom (Ref. 29). These findings are consistent with the view that the compounds shown in Table 3 form excited complexes involving the interaction of the aryl group with two amino groups.

The question arises as to what non-radiative decay routes are available to complexes involving three interacting groups. It is well known that for complexes involving the interaction of two groups (Ref. 31) triplet formation can occur. As to whether the triplet is generated from the encounter or fluorescent exciplex is a matter of some debate. There are some definitive studies in which there is clear evidence for the formation of triplets via the fluorescent exciplex (Ref. 32). In polar solvents, where radical ion formation can take place, triplet formation can also occur via recombination of radical ions (Ref. 33). We have employed nanosecond laser flash photolysis to measure triplet yields for a number of systems which exhibit intramolecular exciplex formation (Table 4). The time resolution of the equipment did not allow us to assess whether the triplets are produced via the fluorescent exciplex. However from the values shown in Table 4 it is apparent that the triplet yield is not directly linked to the quantum yield of exciplex formation and is not particularly

TABLE 4   Quantum yields of triplet formation for compounds exhibiting
            intramolecular exciplex formation.

Compound	Cyclohexane		Tetrahydrofuran		Acetonitrile	
	ϕ_F	ϕ_T	ϕ_F	ϕ_T	ϕ_F	ϕ_T
$Np(CH_2)_2N$ (pentagon)	0.252	0.30	0.043	0.29	0.019	0.29
$Np(CH_2)_2N$ (hexagon)	0.236	0.23	0.062	0.27	0.029	0.43
$Np(CH_2)_2N$ $(CH_2)_{12}$	0.415	0.28	0.140	0.21	0.073	0.38
$NpCH_2NEt_2$	~ 0	0.10	~ 0	0.26	~ 0	0.27
$Np(CH_2)_2NEt_2$	0.406	0.29	0.097	0.33	0.040	0.22
$Np(CH_2)_3NEt_2$	0.200	0.31	0.122	0.32	0.015	0.13
$Np(CH_2)_4NEt_2$	0.034	0.38	-	0.40	0.002	0.08

Np = 1-Naphthyl.

solvent dependent.   On the other hand, the triplet yields for compounds forming complexes
involving three interacting groups (Table 3) show a marked decrease as the solvent polarity
is increased.   Why should this be the case? One may argue that the energy of the radical
ion pair formed by the compounds shown in Table 3 lies below that of the triplet state.
Certainly the ability of the two nitrogen atoms to interact should help to stabilise the

$$\overset{\cdot}{Ar}\!\!-\!\!\overset{\cdot\cdot}{\overset{+}{N}}\!\!-\!\!N\!\!< \quad\longleftrightarrow\quad \overset{\cdot}{Ar}\!\!-\!\!N\!\!-\!\!\overset{\cdot\cdot}{N}\!\!<$$

radical cation.   Another possibility is that the energy of the "excited diamine" lies below
the triplet state of the aromatic hydrocarbon in highly polar solvents.   If either or both
of these explanations are correct, there is the possibility that α,ω-diaminoalkanes will
quench aromatic hydrocarbon triplets in polar solvents.   This was shown to be the case by
studying the quenching of naphthalene and anthracene triplets in cyclohexane and acetonitrile
solution.   These results are shown in Table 5. As can be seen, the quenching is much more
efficient in acetonitrile than in cyclohexane. For acetonitrile solutions the chain length
had little effect upon quenching efficiency whereas in cyclohexane the diaminoethanes are
more effective than the longer chain compounds. Presumably the higher efficiency of
quenching in acetonitrile is due to the greater ability of this solvent to stabilise charged
species.   In the light of the results from the quenching of aromatic hydrocarbon singlet
states by α,ω-diaminoalkanes it is conceivable that the diaminoethanes are better quenchers
than the longer chain diamines in cyclohexane because they form ternary complexes with the
triplet hydrocarbon.

TABLE 5.   Quantum yields of naphthalene and anthracene triplet formation
            in degassed cyclohexane (ϕ_T^C) and acetonitrile (ϕ_T^A) solutions
            containing α,ω-diaminoalkanes (1 x 10^{-2}M).

Amine	n	Naphthalene[a]		Anthracene[a]	
		ϕ_T^C	ϕ_T^A	ϕ_T^C	ϕ_T^A
Pyr(CH$_2$)$_n$Pyr	2	0.38	0.17	-	-
	3	0.55	0.22	0.53	0.30
	6	0.53	0.21	-	-
	8	0.57	0.18	-	-
Pip(CH$_2$)$_n$Pip	2	0.31	0.14	-	-
	3	0.61	0.20	0.61	0.30
	6	0.73	0.32	-	-
	8	0.66	0.37	-	-

a   Based on ϕ_T for naphthalene and anthracene of 0.68 and 0.72 respectively (Ref. 8).

EFFECT OF CONFORMATION UPON INTRAMOLECULAR EXCIPLEX FORMATION

It is well known that there are strict conformational requirements for fluorescent excimer
formation (Ref. 34).   This does not appear to be the case for fluorescent exciplex formation
(Ref. 31 and 35).   The conformational requirements for fluorescent complex formation
(Ref. 36) and fluorescence quenching (Ref. 37) appear to be solvent dependent: they are more
demanding for non polar than for polar solvents.   In an effort to understand conformational
effects upon fluorescent exciplex formation we, and others, have studied compounds of the
type 1, 2 (Ref. 38), 4, 5 and 6 (Ref. 30 and 35) as well as related anthracene compounds
(Ref. 39) and 4-aminobenzonitriles (Ref. 40).

We now report upon compounds 7, 8 and 9 (Ref. 41).
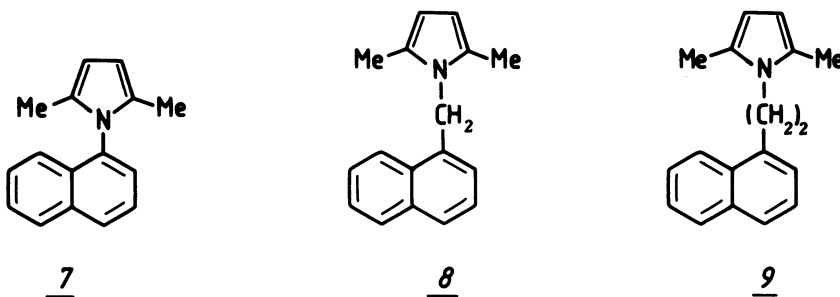
The u.v. absorption spectra of these compounds show that in the ground state there is little
interaction between the pyrrole and naphthalene nucleus.   Although the absorption spectra of
7-9 are hardly affected by a change in solvent polarity their fluorescence spectra are highly
dependent upon this physical property.   Appropriate photophysical parameters are shown in
Table 6.   The wavelengths of exciplex fluorescence for 7-9 in a particular solvent are
remarkably similar.   The energy of an excited complex is given by Equation 4.

$$E_{\mu C} = I - E_A - C - \Delta H_S \qquad \text{eq. 4}$$

($E_{\mu C}$ = Energy of the complex,   I = Ionisation potential, E_A = Electron affinity,
C = Coulombic interaction and ΔH_S = Solvation energy).

TABLE 6   Quantum yields of fluorescence, fluorescence lifetimes and wavelengths
            for maximal exciplex fluorescence for 7-9 in various degassed solvents
            at 20°C.

Solvent	7			8			9		
	λ_{max} (nm.)	τ (ns.)	ϕ	λ_{max} (nm.)	τ (ns.)	ϕ	λ_{max} (nm.)	τ (ns.)	ϕ
Cyclohexane	405	7.2	0.03	398	15.8	0.03	396	36	0.36
Benzene	440	5.0	0.02	412	10.2	0.03	414	75	0.28
Acetonitrile	505	6.9	0.01	490	14.0	0.02	485	41	0.12

Since compounds 7-9 have similar I and E_A values the only difference one might expect to find
in the energetics of complex formation must be due to either the C or the ΔH_S terms.   These
differences are, apparently, very small.   In the case of 7 there will be some perturbation
due to the operation of inductive effects which operate via the σ-bond which connects the
pyrrole with the naphthalene nucleus.

Examination of molecular models shows that 9 can adopt a sandwich conformation in which the
pyrrole ring lies over the naphthalene nucleus.   It is impossible for 7 and 8 to adopt such
a conformation.   Thus although 7-9 can adopt an array of conformations, very few of which are
common to each other, they display similar fluorescence spectra and this suggests that the
conformation of the exciplex does not play a crucial role in determining the extent of charge
transfer in the complex.   Probably what is of significance, is the relative proximity of the
positive and negative charges in the excited complex since this will determine the magnitude
of the Coulombic interaction term.   The other photophysical parameters of 7-9 do appear to be
structurally dependent.   Compound 9 has a relatively high quantum yield of fluorescence in
cyclohexane which drops as the solvent polarity increases.   Both 7 and 8 show low quantum
yields of fluorescence in all the solvents and also their fluorescence lifetimes are conside-
rably shorter than those of 9.   It appears therefore, that the inability of 7 and 8 to adopt
a favourable exciplex conformation leads to low quantum yields of fluorescence and short
fluorescence lifetimes, but does not impair the efficiency with which the pyrrole nucleus
quenches the aromatic hydrocarbon fluorescence.

Since non-radiative decay processes are so important for 7 and 8 the triplet yields of these
compounds and of 9 in various solvents were measured.   The results are summarised in Table 7.
For 7 and 9, there is a gradual reduction in triplet yield as the solvent polarity is

TABLE 7.   Quantum yields of triplet formation for 7, 8 and 9 in various
             degassed solvents at 20°C.

Compound	Cyclohexane	Tetrahydrofuran	Acetonitrile	Methanol
7	0.31	0.33	0.22	0.2
8	0.02	0.04	0.08	0.04
9	0.28	0.32	0.185	0.07

increased.   This suggests that the fluorescent exciplex plays a part in triplet production
but this cannot be the exclusive pathway since the triplet yield of 7 in acetonitrile
(Table 7) is much higher than its fluorescence yield (Table 6) in the same solvent.   The most
peculiar, and therefore well checked result is that triplet production from 8 is remarkably
inefficient.   We can offer no explanation for this behaviour but note that 1-(diethylamino-
methyl)-naphthalene has a low triplet yield in cyclohexane and therefore the origin of the
effect may be one of conformation.

Many compounds undergo conformational changes as a result of excitation e.g. 9,9'-bianthryl
(Ref. 42 and 43) and 1,1'-binaphthyl (Ref. 44 and 45).   The absorption spectrum of 1,1'-bi-
naphthyl indicates that in the ground state, there is little interaction between the two

naphthyl groups. The fluorescence spectrum of this compound exhibits a broad featureless
band which is red-shifted from the naphthalene fluorescence. Since change in solvent
polarity has little effect upon the wavelength of maximal emission the red shift cannot be
ascribed to charge transfer. The lack of structure and the red-shift of the fluorescence
band has been attributed to the initially excited binaphthyl, which has the two naphthyl
groups lying in different planes, relaxing by becoming planar. This conclusion has been
challenged (Ref. 46) and the suggestion made that in the relaxed excited singlet state the
interplanar angle is less than that for the ground state molecule but is not zero. This
conformational change occurs in <280 ps (Ref. 47). Since this relaxation occurs so quickly
it is reasonable to propose that if 1,1'-binaphthyl forms an exciplex with the amine, it will
be the relaxed binaphthyl that participates. The fluorescence of 1,1'-binaphthyl in cyclo-
hexane solution is quenched by the addition of N-(1-propyl)-2,5-dimethylpyrrole and this is
accompanied by a broadening of the tail of the binaphthyl fluorescence (Fig. 5). Even at
high amine concentrations no discreet maximum for the exciplex fluorescence is observable.
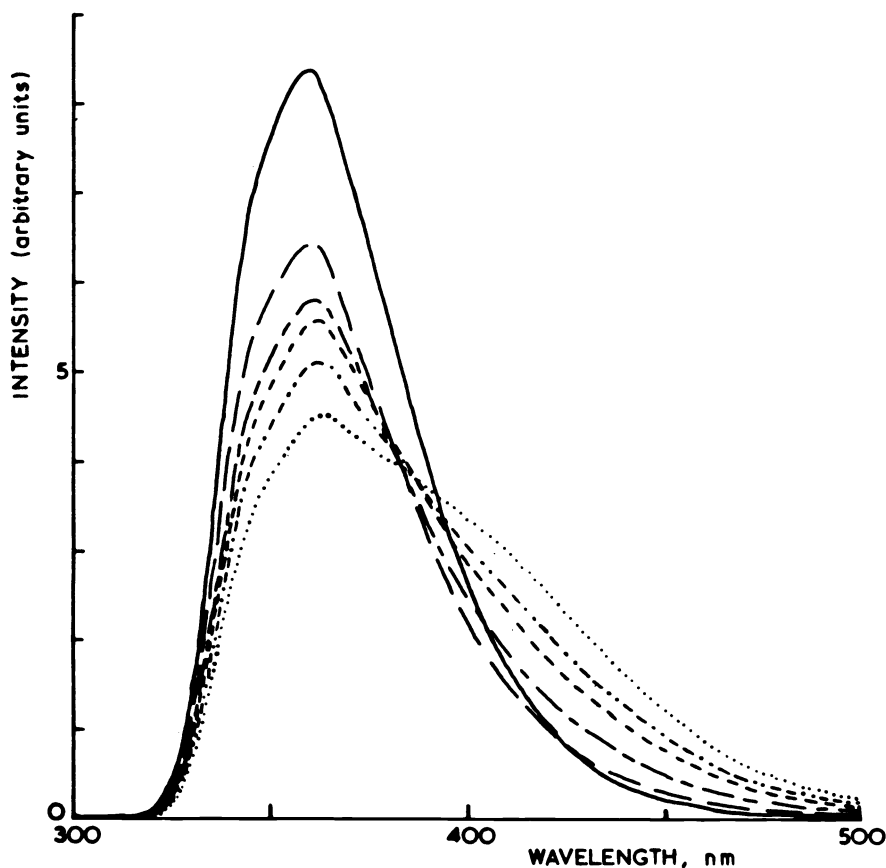

Fig. 5.   Fluorescence spectra of 1,1'-binaphthyl in cyclohexane solution
containing N-(1-propyl)-2,5-dimethylpyrrole at varying concentrations.

When more polar solvents than cyclohexane are used, fluorescence quenching is observed but,
except for benzene, no exciplex fluorescence can be seen. A Stern-Volmer plot for the
quenching in acetonitrile showed that it occurs at the diffusion-controlled rate. The
kinetics of the quenching process in cyclohexane were studied by the technique of time-
correlated single photon counting and it was found that exciplex formation is favoured over
exciplex dissociation, to give the excited monomer, by a factor of approximately 100

$(k_1 = 5.4 \times 10^9 M^{-1} s^{-1}$ and $k_{-1} = 6.5 \times 10^7 s^{-1}$ — see eq. 3).

For the binaphthyl-pyrrole system there are two features worthy of note. Firstly, the wave-
length of the exciplex emission and secondly, the low quantum yields for exciplex fluores-
cence. Rather surprisingly, what little exciplex fluorescence can be observed resembles
that produced by interaction of the excited singlet state of naphthalene with the pyrrole.
If there is extensive delocalisation in the excited singlet state of binaphthyl the reduction

potential of this species should be far lower than that of naphthalene and consequently the exciplex emission should be red shifted relative to that for naphthalene.   We therefore conclude that in the emitting binaphthyl exciplex only one of the naphthalene rings is associated with pyrrole which is in accord with the view that the first excited singlet state of binaphthyl is not planar.   The low quantum yields of exciplex fluorescence may be due to the fact that a conformationally mobile species is a partner in the complex and consequently the excitation energy may be lost non-radiatively by being utilised in bringing about conformational changes.   This situation is somewhat reminiscent of that which obtains for a Dewar benzene when it participates in exciplex formation (Ref. 48) and leads one to question whether the observed exciplex emission is not coming from the initially created exciplex but rather from one in which the binaphthyl has undergone some conformational changes.
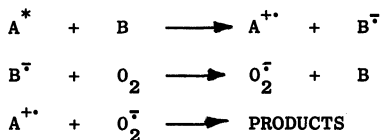
SOLVENT ISOTOPE EFFECTS UPON EXCIPLEX FORMATION AND DECAY PROCESSES

Many compounds which contain a donor and acceptor group linked by a flexible insulating chain, exhibit exciplex fluorescence in polar solvents such as acetonitrile and alcohols (Ref. 5, 30, 31, 36 and 41).   Since it is known that radical anions, generated in photochemical reactions, can be protonated, it seemed of interest to determine whether exciplexes can also be protonated and whether this provides another mechanism for non-radiative decay.   The fact that the triplet yield for 9 (Table 7) is much lower in methanol than acetonitrile could be due to the relaxed exciplex undergoing protonation and hence reducing the efficiency of triplet production.   The quantum yields of unquenched naphthalene fluorescence and exciplex fluorescence for a series of naphthylalkyl amines in methanol and deuterated methanol (CH_3OD) were

measured and results are shown in Table 8.   From measurements of the quantum yields of unquenched naphthalene fluorescence it can be seen that the quenching of naphthalene fluorescence is more efficient in the deuterated solvent.   We believe that this reflects the abilities of the two solvents to bond to the lone pair electrons of the amino groups.   This type of bonding raises the ionisation potential of the amine and consequently decreases the ability of the amine to participate in electron transfer reactions (Ref. 49).   The quenching studies suggest that methanol bonds to the amine (via hydrogen bonding) more strongly than the deuterated alcohol.   As one might expect, this type of effect is less noticeable for aromatic amines than for aliphatic amines.   The effect of the solvent interacting with the ground state amine appears to be reflected in the quantum yields of exciplex formation. However the higher yield of exciplex in the deuterated solvent may not be exclusively due to the ground state amine-solvent interactions but rather be a reflection of the deuterated solvent being a less effective quencher of the exciplex (by deuteration) than the protic solvent.   That the solvent plays a part in the decay processes is shown by the fact that the exciplexes have longer lifetimes in the deuterated than in the protic solvents (Table 8) (Ref. 50).

Table 8 also gives the quantum yields of triplet formation.   In all cases the yields are higher in the deuterated solvent as is of course the quantum yield of exciplex fluorescence. This suggests that at least some triplet formation occurs via the relaxed exciplex, in highly polar solvents, and that protonation of exciplexes can interfere with triplet production.

ELECTRON TRANSFER PROCESSES IN PHOTO-OXIDATION REACTIONS

It has been recognised that many photo-oxidation reactions involve electron transfer processes.   In some cases the initiation is an electron transfer process.   In other cases,

$$A^* + B \longrightarrow A^{+\cdot} + B^{\overline{\cdot}}$$

$$B^{\overline{\cdot}} + O_2 \longrightarrow O_2^{\overline{\cdot}} + B$$

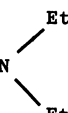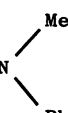$$A^{+\cdot} + O_2^{\overline{\cdot}} \longrightarrow PRODUCTS$$

singlet oxygen, generated in a conventional manner, appears to react via an electron transfer process e.g. with amines (Ref. 51) and the azide ion (Ref. 52).

A very fashionable and valuable method for determining whether a photo-oxidation reaction occurs via singlet oxygen involves measuring the rate of reaction in a non-deuterated solvent and in a corresponding deuterated solvent (Ref. 53).   The lifetime of singlet oxygen is usually longer in the deuterated solvent (Ref. 54) and consequently if certain conditions are fulfilled the rate of oxidation is higher in the deuterated than in the non-deuterated solvent (Ref. 55).   From the preceeding section it can be seen that changing the solvent, from one containing O-H bonds to one containing O-D bonds, can lead to a change in photophysical parameters.   In particular this change can affect electron transfer reactions

TABLE 8 Quantum yields of unquenched naphthalene and exciplex fluorescence, exciplex fluorescence lifetimes and quantum yields of triplet formation for some naphthylalkylamines in degassed methanol and deuterated methanol (CH$_3$OD) at 20°C.

(A)

Compound	n	Methanol				Deuterated Methanol			
		ϕ_{Np}	ϕ_{EX}	ϕ_T	τ_{EX}(ns)	ϕ_{Np}	ϕ_{EX}	ϕ_T	τ_{EX}(ns)
Np(CH$_2$)$_n$N(Et)(Et)	2	0.06	0.019	0.13	5.6	0.029	0.025	0.17	8.3
	3	0.009	0.001	0.07	3.4	0.003	0.003	0.09	4.6
Np(CH$_2$)$_n$N(Me)(Ph)	2	<0.001	0.043	0.11	23.8	<0.001	0.056	0.14	32.1
	3	0.007	0.023	0.11	11.6	0.006	0.039	0.19	22.8
	4	0.006	0.004	0.12	11.6	0.005	0.006	0.23	19.5

(B)

Compound	n	$\dfrac{\phi_{Np}^{MeOH}}{\phi_{Np}^{MeOD}}$	$\dfrac{\phi_{EX}^{MeOD}}{\phi_{EX}^{MeOH}}$	$\dfrac{\phi_T^{MeOD}}{\phi_T^{MeOH}}$	$\dfrac{\tau_{EX}^{MeOD}}{\tau_{EX}^{MeOH}}$
Np(CH$_2$)$_n$N(Et)(Et)	2	2.07	1.31	1.31	1.48
	3	3.0	3.0	1.29	1.35
Np(CH$_2$)$_n$N(Me)(Ph)	2	–	1.3	1.27	1.35
	3	1.17	1.69	1.73	1.96
	4	1.2	1.50	1.92	1.68

Np = 1-naphthyl.

involving lone pairs that interact with the solvent. Thus it would seem that any systems involving amines may show isotope effects that are out of proportion to those exhibited by compounds such as alkenes.

Recently we have been employing the solvent isotope effect to distinguish between reactions involving singlet oxygen and electron transfer processes and found, to our surprise, that the magnitude of the isotope effect is dependent upon the nature and concentration of the sensitising dye (Table 9). As can be seen from Table 9, the isotope effect is reduced as the concentration of the sensitiser is increased. This observation can be explained by postulating that the dyes act as quenchers for singlet oxygen. Recently, it has been concluded that chlorophyll acts as a quencher for singlet oxygen (Ref. 56). For the solvent isotope effect to be maximal:

$$k_d \gg k_r[\text{Subst.}] + k_q[\text{Sens.}]$$

where k_d = unimolecular decay constant for singlet oxygen.

k_r = rate constant for reaction of singlet oxygen with the substrate at a concentration [Subst.].

k_q = bimolecular rate constant for quenching of singlet oxygen by the sensitiser at a concentration [Sens.].

The fact that the isotope effects shown in Table 8 are sensitive to the dye concentration suggests that $k_d \sim k_q$ [Sens.]. The ruthenium complex employed as a sensitiser is interesting in that its photophysical properties (e.g. ϕ_{Lumin}, τ_{Lumin}) are known to be affected by change from a protic to the corresponding deuterated solvent (Ref. 57). As a consequence of these effects, the isotope effects observed with this sensitiser should be different to those obtained with other sensitisers whose photophysical properties do not alter with such a solvent change e.g. Rose Bengal.

TABLE 9   Effect of type and concentration of dye upon the solvent isotope effect determined for the photo-oxygenation of (+)-limonene (5×10^{-3} M) in acetonitrile/water and acetonitrile/deuterium oxide (1:1 V/V) mixtures.

Dye	Concentration (M)	Isotope Effect
Rose Bengal (Eastman-Kodak)	7.86×10^{-4}	2.18
	1×10^{-5}	3.2
Methylene Blue (Aldrich)	2.14×10^{-3}	1.79
	1×10^{-5}	3.68
Thionine (Koch-Light)	2.78×10^{-3}	2.12
	5×10^{-5}	6.08
Tris-ruthenium (II) (2,2'-bipyridyl) chloride	1×10^{-3}	2.75
	1×10^{-4}	5.32

Since the triplet energies of the sensitisers lie above the energy of singlet oxygen it is unlikely that the quenching of singlet oxygen by the ground state dye is an energy transfer process. All the sensitisers employed in this study are potential electron donors (particularly methylene blue and thionine which are aromatic amines) and it is possible therefore that the quenching is an electron transfer process. If this is the case, the term k_q [Sens.] will be affected by a change from a protic solvent to its deuterated counterpart.

CONCLUSIONS

(i)   OPPORTUNITIES

The exploration of the photophysics of electron transfer processes has revealed a wide variety of intermediates that can undergo chemical reaction. In the last few years many chemical reactions of these species have been identified.

An area which has received less attention is the use of electron transfer processes to quench the excited singlet state with the object of producing triplet states. Such a process could be invaluable where it is impossible to carry out classical sensitisation studies and hence positively identify a triplet state as a reactive intermediate. The external heavy atom effect may be an example of an electron transfer process giving rise to triplets but as yet there is no direct evidence for the participation of an electron transfer process.

The ability of certain compounds e.g. α,ω-diaminoalkanes to act as quenchers for both excited singlet and triplet states could be the basis for the development of effective anti-oxidants. The commercial success of some hindered piperidines as anti-oxidants may have its origins in their ability to quench both types of excited states. The remarkable sensitivity of exciplex production to a change from a protic solvent to its deuterated analogue, could prove useful in examining solvent properties. Fluorescence measurements appear to offer a very sensitive technique for probing such parameters.

(ii) PITFALLS

Throughout the paper, the difficulty of making rigorous mechanistic assignments has been emphasised. For example, in the case of triplet production, it is clear that the relaxed

exciplex plays a part but this is clearly not the sole pathway. It appears that besides radical ion combination, the non-relaxed exciplex can also participate. The finding that relaxed exciplexes can be protonated means that the observation of deuterium incorporation in a product can no longer be taken as unequivocal evidence for the participation of radical ions in these reactions.

The described work emphasises the need for caution in interpreting solvent isotope effects. It would appear that there is a need for a greater understanding of solvent isotope effects upon basic photophysical processes.

The occurrence of ternary complexes and the fact that these alter the photophysics of a system in quite a dramatic way shows that conclusions concerning mechanisms can only be drawn when concentration effects are taken into account. Thus the use of an addend at a concentration of $> 10^{-2}$ has the potential for aiding the involvement of ternary complexes. Although these species may not participate in product formation, they could lead to a diminution in the efficiency of production of the desired product.

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