THE EFFECT OF ADDED SALTS ON ELECTRON TRANSFER REACTIONS INVOLVING EXCIPLEXES: THE N,N-DIMETHYLANILINE-PHOTOSENSITIZED DECHLORINATION OF 4-CHLOROBIPHENYL

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Summary

The dechlorination of 4-chlorobiphenyl (ClBi) photosensitized by N,N-dimethylaniline (DMA) was studied in methanolic and ethyl acetate solutions by means of continuous photolysis at 313 nm. The hydrogen chloride quantum yield was measured as a function of ClBi concentration. The reaction proceeds mainly via DMA singlet state sensitization.

Excited singlet deactivation of DMA by ClBi was investigated by fluorescence quenching. In low polarity solvents such as cyclohexane and ethyl acetate, the fluorescence quenching was accompanied by the appearance of the fluorescence band of an exciplex. The fluorescence quenching of the DMA–ClBi exciplex by tetrabutylammonium perchlorate and lithium perchlorate was also studied. Both salts enhanced the sensitized dechlorination of ClBi and an electrostatic interaction between undissociated perchlorates and the exciplexes is postulated to be responsible for the enhanced dechlorination.

1. Introduction

Photoinduced electron transfer reactions between electron donor (D) and acceptor (A) molecules in polar solvents have been the subject of considerable mechanistic and synthetic interest. In these reactions, the separation of the initially formed radical ion pair ($A^{\bar{\cdot}} \cdots D^{\dot{+}}$) into free ions $A^{\bar{\cdot}}$ and $D^{\dot{+}}$ is inhibited because of the occurrence of competitive back electron transfer.

Consequently, a target of the research on photoredox systems is to suppress back electron transfer. Use of coulombic effects to prevent back electron transfer is an effective approach, as shown by photoinduced electron transfer in micellar and/or polyelectrolyte solutions [1 - 6].

Exciplex intermediates play an important role in electron transfer reactions. However, it is only recently that coulombic effects have been employed

in investigations on exciplexes, and the fluorescence quenching of exciplexes by quaternary ammonium salts has been studied [7 - 9].

A flash photolysis study of the exciplex formed between pyrene and 1,4-dicyanobenzene in dimethoxyethane revealed that the amount of pyrene cation radical formed increases when the exciplex is quenched by a quaternary ammonium salt [10].

Electron transfer reactions in polar solvents are affected by quaternary ammonium salts. Thus, the efficiency of the 9,10-dicyanoanthracene-sensitized cis–trans photoisomerization of 1,2-diphenylcyclopropanes is enhanced remarkably by these salts [11].

In previous work [12] we showed that electronically excited dimethylaniline (DMA) sensitizes the dehalogenation of dichlorobenzenes by a mechanism which involves electron transfer from both the excited singlet and the triplet states of the DMA. The triplet states of dichlorobenzenes are higher in energy than that of DMA. When the halobenzene has a triplet state with lower energy than DMA (energy, 3.28 eV) [13] the electron transfer from the triplet state is expected to compete with quenching of triplet DMA by energy transfer.

In this paper we report a kinetic study of the photodechlorination of 4-chlorobiphenyl (ClBi) (triplet energy, 2.82 eV) [14] sensitized by DMA. It was found that energy transfer prevails over electron transfer from the triplet state. Evidence is also presented which supports the formation of an exciplex between DMA and ClBi as an intermediate in the electron transfer. The exciplex quenching and the enhanced dechlorination by tetrabutylammonium perchlorate (TBAP) and lithium perchlorate were studied. The results, we believe, are further evidence of the alteration in the behavior of exciplexes by quaternary ammonium salts.

2. Experimental details

DMA (Merck) was distilled at reduced pressure just prior to use. ClBi (Pfaltz and Bauer) was recrystallized several times from ethanol. Its purity was checked by gas liquid chromatography.

Lithium perchlorate (G. Frederick Smith) was used as received. TBAP was prepared from tetrabutylammonium bromide (Fluka) and perchloric acid (Carlo Erba) and recrystallized from ethyl acetate–n-hexane mixtures.

Steady state photolysis of DMA (0.1 M solutions in methanol or ethyl acetate) and different amounts of ClBi were carried out at 313 nm in sealed Pyrex ampoules within a merry go round. The 313 nm lines of a medium pressure mercury lamp were isolated with an alkaline potassium chromate solution.

Chloride ion produced by photolysis was measured with an Orion specific ion electrode. The conversion of ClBi was always kept below 2%. The DMA-sensitized dechlorination of chlorobenzene was used for the actinometry [12].

Fluorescence measurements were performed with an Aminco–Bowman spectrofluorometer. In order to match the photolysis experimental conditions, a front-surface optical arrangement was used. Because of the high quantum yield of sensitized dechlorination, special care was taken in obtaining the fluorescence spectra. The minimum excitation light intensity was used, as otherwise the emission spectra of the exciplexes would have been masked by the spectrum of an unidentified product.

3. Results and discussion

3.1. The exciplex between N,N-dimethylaniline and 4-chlorobiphenyl

When excited at 310 nm, DMA shows a fluorescence spectrum with a maximum at 335 nm in cyclohexane and 345 nm in methanol [15]. Halobenzenes quench this fluorescence, and in cyclohexane a red shift of the emission is also seen. Since no change was detected in the absorption spectrum, the shift was ascribed to the formation of an exciplex between DMA and the halobenzene [12, 15].

With ClBi as quencher, the above effect is more pronounced. When a cyclohexane solution of DMA is irradiated in the presence of ClBi, the fluorescence quenching of DMA is accompanied by the appearance of a new fluorescence band. This new band is red shifted and broader than the DMA fluorescence band and is typical of exciplex emission. The spectra of the exciplexes formed in cyclohexane and ethyl acetate are shown in Figs. 1 and 2 respectively. The formation of an exciplex between DMA and biphenyl (Bi) has been previously reported [16] and we also observed this exciplex. Both exciplexes were quenched in more polar solvents and they could not be observed in methanol or acetonitrile.
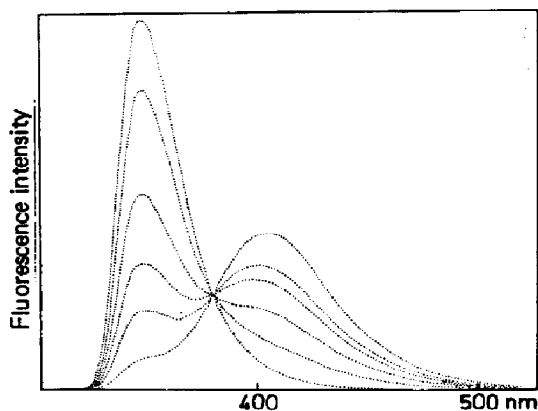

Fig. 1. Spectra of the exciplex between N,N-dimethylaniline and chlorobiphenyl in cyclohexane (chlorobiphenyl concentrations: 0, 0.0065, 0.021, 0.044, 0.076 and 0.20 M).
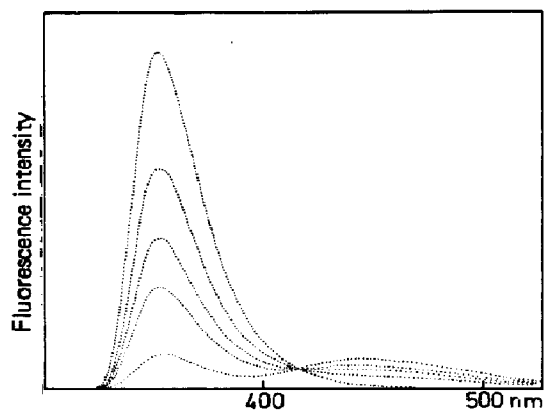
Fig. 2. Spectra of the exciplex between N,N-dimethylaniline and chlorobiphenyl in ethyl acetate (chlorobiphenyl concentrations: 0, 0.015, 0.036, 0.062 and 0.20 M).

TABLE 1

Quenching of N,N-dimethylaniline fluorescence by 4-chlorobiphenyl and biphenyl

Solvent	4-Chlorobiphenyl		Biphenyl	
	k_{SV} (M^{-1})	k_q $(\times 10^{-10} M^{-1} s^{-1})$	k_{SV} (M^{-1})	k_q $(\times 10^{-10} M^{-1} s^{-1})$
Cyclohexane	34 ± 3	1.4	25 ± 2	1.0
Ethyl acetate	43 ± 5	1.8	28 ± 1	1.2
Methanol	45 ± 4	1.6	30 ± 1	1.1
Acetonitrile	45 ± 4	1.8	—	—

The Stern–Volmer (k_{SV}) and bimolecular (k_q) constants for quenching of DMA fluorescence by ClBi and Bi in different solvents are given in Table 1. The bimolecular quenching rate constants were obtained with the assumption of a fluorescence lifetime $^1\tau_0$ of 2.8 ns in polar solvents and 2.4 ns in the less polar solvents, these being values given by Berlman [17] in ethanol and cyclohexane respectively.

We considered the rate constants in Table 1 to be accurate only to 10%. Nevertheless, it is clear that the fluorescence quenching constants are all within the diffusional limit. According to the redox potentials of DMA (0.78 V) [18], Bi (−2.41 V) and ClBi (−2.06 V) [19], this may be interpreted as the consequence of a highly exergonic electron transfer process in the excited state.

3.2. Quenching of the exciplex by salts

We also studied the quenching of the exciplex by added salts. In order to observe this effect it is necessary to use a solvent of polarity sufficiently low that the emission can be observed but not so low that the salt cannot be dissolved. Ethyl acetate fulfils this requirement.

The salts employed were TBAP and lithium perchlorate. The fluorescence of DMA in ethyl acetate is unaffected by these salts but the emission of the DMA–Bi and DMA–ClBi exciplexes is quenched by the salts. Also, the emission maximum is slightly shifted to the red when the concentration of TBAP is increased (Fig. 3).

Stern–Volmer analysis of the exciplex quenching shows linear behavior in a reduced concentration range of the salt (inset, Fig. 3), and then the plot shows a small downward curvature. This curvature has been previously observed in the quenching of other exciplexes [8, 10], and has been ascribed to the formation of TBAP aggregates. Similar behavior is observed with lithium perchlorate as the quencher (Fig. 4).

From the initial slopes of the Stern–Volmer plots the k_{SV} constants for the exciplex quenching were obtained. Values of these constants are given in Table 2.
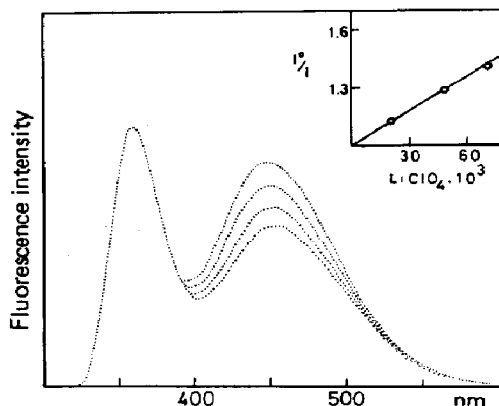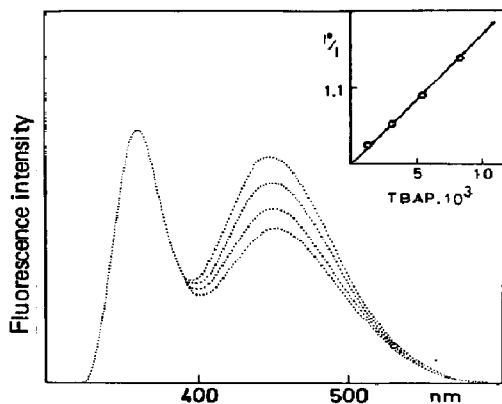
Fig. 3. Quenching of the N,N-dimethylaniline–chlorobiphenyl exciplex in ethyl acetate by tetrabutylammonium perchlorate. The Stern–Volmer plots are shown in the inset.

Fig. 4. Quenching of the N,N-dimethylaniline–chlorobiphenyl exciplex in ethyl acetate by lithium perchlorate. The Stern–Volmer plots are shown in the inset.
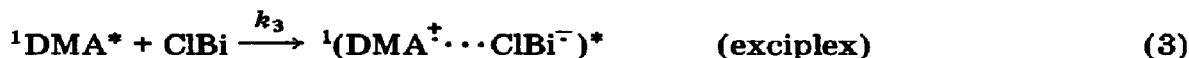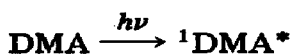
TABLE 2

Fluorescence quenching of DMA–biphenyl exciplexes by added salts

Exciplex	k_{SV} (M^{-1})	
	TBAP	Lithium perchlorate
DMA–Bi	18 ± 2	5.1 ± 0.3
DMA–ClBi	17 ± 1	5.8 ± 0.3

Since the salts used in this study do not possess electron-donating or electron-accepting ability, the exciplex quenching cannot be explained in terms of a charge transfer interaction between exciplexes and the salts.

3.3. The photosensitized dechlorination of 4-chlorobiphenyl

When solutions of DMA in methanol or ethyl acetate were irradiated at 313 nm in the presence of ClBi, hydrogen chloride was produced. A double reciprocal plot of the experimental results, i.e. the inverse of the hydrogen chloride quantum yield vs. the inverse of the concentration of ClBi, is shown in Fig. 5 for ethyl acetate and methanolic solutions. The results can be explained by the following reaction scheme:

$$DMA \xrightarrow{h\nu} {}^1DMA^*$$

$${}^1DMA^* \xrightarrow{k_1} DMA + h\nu \tag{1}$$

$${}^1DMA^* \xrightarrow{k_2} {}^3DMA^* \tag{2}$$

$${}^1DMA^* + ClBi \xrightarrow{k_3} {}^1(DMA^{\overset{+}{\cdot}} \cdots ClBi^{\overline{\cdot}})^* \qquad \text{(exciplex)} \tag{3}$$

$$\text{Exciplex} \xrightarrow{k_4} \text{DMA} + \text{ClBi} \qquad (4)$$

$$\text{Exciplex} \xrightarrow{k_5} \text{DMA}^{\ddagger} + \text{Cl}^- + \text{Bi}^{\bullet} \qquad (5)$$

$$\text{Exciplex} \xrightarrow{k_6} \text{DMA} + \text{ClBi} + h\nu' \qquad (6)$$

In the above reaction scheme exciplex fluorescence appears only when the solvent has a low polarity. Reaction (6) does not occur in solvents such as methanol or acetonitrile, and in these solvents reaction (3) probably involves complete electron transfer from DMA to ClBi.
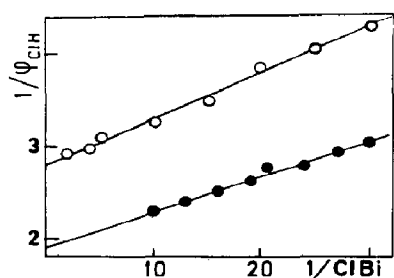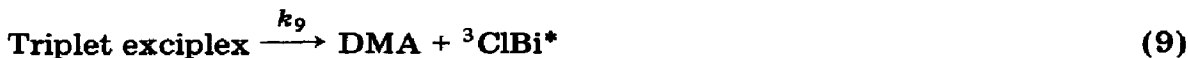

Fig. 5. Plot of the inverse of the hydrogen chloride quantum yield *vs.* the inverse of the chlorobiphenyl concentration in ethyl acetate (○) and methanol (●).

Taking into account the high quantum yield of the DMA triplet state [12] and the fact that the triplet state of DMA could also sensitize the decomposition of ClBi by electron transfer, the following reactions must be considered:

$$^3\text{DMA}^* \xrightarrow{k_7} \text{DMA} \qquad (7)$$

$$^3\text{DMA}^* + \text{ClBi} \xrightarrow{k_8} \text{triplet exciplex} \qquad (8)$$

$$\text{Triplet exciplex} \xrightarrow{k_9} \text{DMA} + {}^3\text{ClBi}^* \qquad (9)$$

$$\text{Triplet exciplex} \xrightarrow{k_{10}} \text{DMA}^{\ddagger} + \text{Cl}^- + \text{Bi}^{\bullet} \qquad (10)$$

$$\text{Triplet exciplex} \xrightarrow{k_{11}} \text{DMA} + \text{ClBi} \qquad (11)$$

Reaction (9) followed by homolytic dechlorination of triplet ClBi is another possible source of hydrogen chloride; however, this extra source may be discarded owing to the very low decomposition quantum yield of ClBi under direct photolysis [20, 21], irrespective of the high triplet yield of excited ClBi.

Triplet DMA might also be quenched by ClBi through an electron transfer mechanism (reaction (10)). This reaction is another source of hydrogen chloride, as observed in the DMA-sensitized dechlorination of dichlorobenzenes [12].

Kinetic analysis of reactions (1) - (11) leads to the following equation:

$$\Phi_{\text{ClH}} = \frac{\varphi_s}{1 + 1/k_3{}^1\tau_0[\text{ClBi}]} + \frac{\varphi_t\varphi_{\text{isc}}}{(1 + k_3{}^1\tau_0[\text{ClBi}])(1 + 1/k_8{}^3\tau_0[\text{ClBi}])} \qquad (I)$$

where $\quad {}^1\tau_0 = (k_1 + k_2)^{-1}, \quad \varphi_s = k_5/(k_4 + k_5 + k_6), \quad {}^3\tau_0 = (k_7)^{-1}$ and $\quad \varphi_t = k_{10}/(k_9 + k_{10} + k_{11})$.

Land *et al.* [22] reported that Bi quenches the triplet state of DMA with a diffusion-controlled rate constant. It is known that the triplet lifetime of DMA is longer than 500 ns [12, 23] and that the triplet state level of ClBi is lower than that of DMA by around 10 kcal mol^{-1}; therefore at the working concentrations of ClBi, the DMA triplet will be completely quenched (reaction (8), followed by reactions (9) - (11)). Hence the contribution of the triplet state of DMA to the production of hydrogen chloride will be negligible only when φ_t approaches zero. Under this limiting condition, eqn. (I) reduces to

$$\Phi_{\text{ClH}} = \frac{\varphi_s}{1 + 1/k_3{}^1\tau_0[\text{ClBi}]} \qquad (II)$$

which can be written as

$$\frac{1}{\Phi_{\text{ClH}}} = \frac{1}{\varphi_s} + \frac{1}{\varphi_s}k_3{}^1\tau_0[\text{ClBi}] \qquad (III)$$

Since the double inverse plots are linear in the concentration range studied (Fig. 5) and the $k_3{}^1\tau_0$ values obtained from the intercepts and slopes of the plots (Table 3) are nearly the same as those obtained by fluorescence quenching methods, the contribution of reactions (8) - (11) to the hydrogen chloride yield is less than 10% of the total.

TABLE 3

Kinetics parameters for the DMA-photosensitized decomposition of ClBi

Solvent	φ_s	$k_3{}^1\tau_0$ (M^{-1})
Methanol	0.52 ± 0.03	51 ± 7
Ethyl acetate	0.36 ± 0.01	57 ± 3

The above result suggests that energy transfer (reaction (9)) is more efficient than electron transfer (reaction (10)) in deactivating the triplet exciplex. The importance of reaction (11) may be disregarded because it is spin forbidden, and as in electron transfer between DMA and chlorobenzenes chloride ion should be produced with an efficiency of unity [12].

A previous study of the photolysis of DMA in the presence of ClBi was carried out by Bunce and Gallacher [24] in methanolic solutions. Their results were obtained over a concentration range two orders of magnitude more dilute than that in our experiments, where the contribution of the

triplet state is predominant. Their results also show that energy transfer is more important than electron transfer in quenching the triplet state of DMA.

For the sake of simplicity, and regardless of the possible small contribution of DMA triplet state to hydrogen chloride production, in Section 3.4 we shall adopt the limiting form of eqn. (I), *i.e.* eqn. (III).

With reference to Table 3, the high values of φ_s in both solvents should be noted. φ_s is the efficiency of formation of free ions in the electron transfer process. The high efficiency observed is in accord with previous results on other chloroaromatics [12], and can also be ascribed to a very fast decomposition of the hypothetically formed ClBi anion radical into Bi radical plus chloride ion.

3.4. Photolysis in the presence of added salts

When an ethyl acetate solution of DMA plus ClBi was photolyzed in the presence of TBAP, there was an increase in the amount of hydrogen chloride formed. The experimental results are shown in Fig. 6 as a plot of the hydrogen chloride quantum yield *vs.* the concentration of TBAP. It can be seen that the hydrogen chloride quantum yield increases smoothly with the concentration of TBAP.
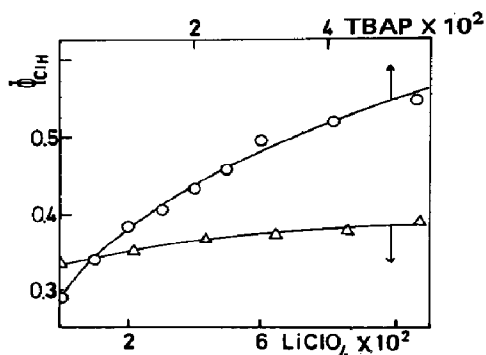

Fig. 6. Plots of hydrogen chloride quantum yield *vs.* the concentration of added salts: O, TBAP (initial chlorobiphenyl concentration, 0.084 M); △, lithium perchlorate. (initial chlorobiphenyl concentration, 0.167 M).

Since TBAP quenches the fluorescence of the DMA–ClBi exciplex it is reasonable to suppose that the quenching is responsible for the enhanced dechlorination of ClBi. To take into account this reactive quenching we propose the following mechanism:

$$\text{Exciplex} + \text{TBAP} \xrightarrow{k_{12}} (\text{exciplex:TBAP}) \ (Z) \tag{12}$$

$$Z \xrightarrow{k_{13}} \text{DMA}^+ + \text{Cl}^- + \text{Bi}^\cdot + \text{TBAP} \tag{13}$$

$$Z \xrightarrow{k_{14}} \text{DMA} + \text{ClBi} + \text{TBAP} \tag{14}$$

A steady state analysis of the reaction scheme involving reactions (1) - (6) and (12) - (14) gives the following equation for the hydrogen chloride quantum yield in the presence of TBAP:

$$\Phi_{ClH} = \frac{k_3{}^1\tau_0[ClBi]}{1 + k_3{}^1\tau_0[ClBi]} \frac{\varphi_s + \{k_{13}/(k_{13} + k_{14})\}k_{12}{}^e\tau_0[TBAP]}{1 + k_{12}{}^e\tau_0[TBAP]} \qquad (IV)$$

where $^e\tau_0 = (k_4 + k_5 + k_6)^{-1}$ and $\varphi_s = k_5{}^e\tau_0$.

The proposed kinetic scheme is the simplest which can explain the experimental evidence. Equation (IV) was used to fit the results given in Fig. 6.

With the known values $k_3{}^1\tau_0$ and φ_s (Table 3), least-squares analysis of eqn. (IV) was performed in which $k_{12}{}^e\tau_0$ and $k_{13}/(k_{13} + k_{14})$ remained adjustable parameters. The best fit to the experimental results was obtained for $k_{12}{}^e\tau_0 = 21$ M. This value is in reasonable agreement with the Stern–Volmer constant obtained for the fluorescence quenching of the exciplex by TBAP (Table 2). For $k_{13}/(k_{13} + k_{14})$ a value of unity was obtained. This means that the quenching of the exciplex by TBAP is highly efficient in assisting the dechlorination of ClBi.

Figure 6 also shows results for the enhanced dechlorination of ClBi in ethyl acetate solutions in the presence of lithium perchlorate. Here it can be observed that lithium perchlorate is less efficient than TBAP in assisting the sensitized dechlorination of ClBi, consistent with the exciplex fluorescence quenching results. In Table 4 the parameters for the best fit of eqn. (IV) to the experimental results are summarized.
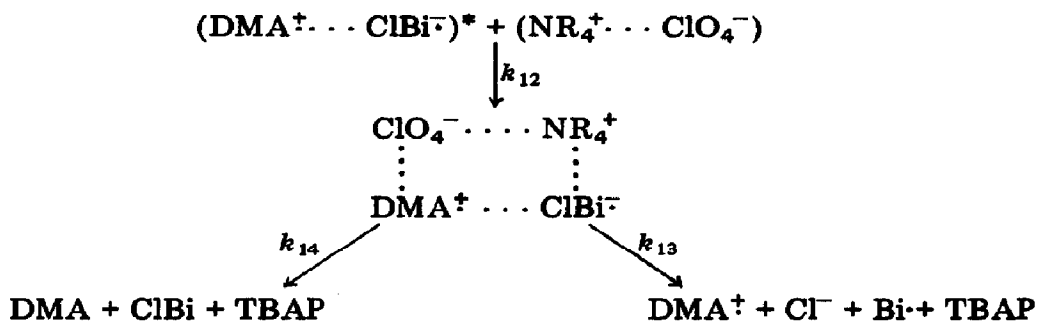
TABLE 4

Kinetics parameters for the exciplex–salt interaction

Salt	$k_{12}{}^e\tau_0$ (M^{-1})	$k_{13}/(k_{13} + k_{14})$
TBAP	21 ± 2	1.0
Lithium perchlorate	7 ± 3	0.5

3.5. Quenching mechanism of the exciplex

There are two questions which still remain: (a) why the exciplex is quenched by perchlorates and (b) why the quenching is reactive, enhancing the photosensitized dechlorination of ClBi.

The first question can be answered on the basis of electrostatic models previously proposed for exciplex quenching by quaternary ammonium salts [7, 8, 10]. Bulky ions form contact ion pairs in aprotic solvents of low dielectric constant. Using the equation derived by Fuoss [25], it can be estimated that most of the TBAP is in the form of ion pairs with ethyl acetate as the solvent. These ion pairs are believed to be the quenching species [7, 8, 10]. Probably an ionic pair associates with the exciplex to form an intermediate complex with the characteristics of a quadrupole. This quadrupole in due

$$(DMA^{\ddagger} \cdots ClBi^{\bar{\cdot}})^{*} + (NR_4^{+} \cdots ClO_4^{-})$$

$$\downarrow k_{12}$$

$$ClO_4^{-} \cdots NR_4^{+}$$

$$\vdots \qquad \vdots$$

$$DMA^{\ddagger} \cdots ClBi^{\bar{\cdot}}$$

$$k_{14} \swarrow \qquad \searrow k_{13}$$

DMA + ClBi + TBAP $DMA^{\ddagger}$ + Cl^{-} + Bi$\cdot$+ TBAP

Scheme 1.

course could evolve towards products (dechlorination) or return to the starting materials according to Scheme 1.

An answer to the second question may be formulated as follows. Since TBAP and lithium perchlorate are stable to oxidation and reduction and have no low-lying excited states, quenching via electron transfer or energy transfer can be ignored. The salts probably change the geometry of the exciplex by forming the quadrupole given in Scheme 1, enlarging the separation of the exciplex components and transforming the exciplex into a solvent-shared ion pair.

As a consequence of the geometrical changes, the extent of back reaction to reactants is reduced and the probability of decomposition of the radical anion is increased.

It is interesting to comment at this point that the enhancement effect of TBAP was not observed in the case of chlorobenzene. This failure of TBAP is concomitant with the lack of a clear chlorobenzene–DMA exciplex emission in non-polar solvents. This probably implies that the exciplex decay is very fast. So, bimolecular quenching by TBAP and therefore also quadrupole formation do not compete with the exciplex decay.

Acknowledgments

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