THE *N,N*-DIMETHYLANILINE-PHOTOSENSITIZED DECHLORINATION OF CHLOROBENZENES

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Summary

The *N,N*-dimethylaniline-(DMA)-photosensitized dechlorination of monochlorobenzene, *ortho-*, *meta-* and *para*-dichlorobenzene and 3,4-dichlorotoluene was studied in methanolic solutions by means of continuous photolysis at 313 nm. Excited singlet deactivation of DMA by the chloro compounds was investigated by fluorescence quenching. Rate constants for triplet quenching were determined by laser flash photolysis.

The quantum yield of formation for hydrogen chloride was measured as a function of the halobenzene concentration. A mechanism was proposed which takes into account electron transfer from both singlet and triplet excited states of DMA. The efficiency of the geminate radical pair to dissociate into free ions was estimated. A value near unity was found when the triplet state of DMA was the radical pair precursor.

1. Introduction

The photochemistry of chlorinated aromatic compounds is a topic of current interest because of the importance of some of these compounds as environmental pollutants.

In some cases, irradiations in the presence of aliphatic amines and dienes have led to enhanced photolability of the halide, as a result of electron transfer reactions [1].

Photochemically induced electron transfer between dialkylamines and aryl halides is well documented. *N,N*-Dimethylaniline (DMA) has already been shown to sensitize the decomposition of several chlorobenzenes [2], chlorobenzene, bromobenzene and iodobenzene [3], chlorobiphenyls [4] and also dichlorodiphenyltrichloroethane (DDT) [5].

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UV irradiation ($\lambda = 313$ nm) of a mixture of DMA and a halobenzene leads to exciplex formation between the excited state of the amine and the halobenzene, followed by electron transfer from the amine. The fluorescence of the DMA is quenched by this process and decomposition of the halobenzene radical anion yields a phenyl radical and hydrogen halide [3].

In the present paper we wish to report evidence that not only the singlet state of DMA is responsible for hydrogen chloride formation but that the triplet state of DMA is almost as efficient as the singlet state in sensitizing the dechlorination of some chlorobenzenes. A general mechanism could be established for this type of reaction which takes into account the different rate constants for the triplet and singlet reactions allowing interpretation of the different photochemical behaviour of the chlorobenzenes.

2. Experimental details

Chlorobenzene (Merck) was freed of thiophenes and then low pressure distilled. 1,2-Dichlorobenzene (Aldrich), 1,3-dichlorobenzene (Fluka) and 3,4-dichlorotoluene (Aldrich) were trap-to-trap distilled. 1,4-Dichlorobenzene (Fluka) was vacuum sublimed. Their purity was determined by gas—liquid chromatography.

DMA (Merck) was distilled at reduced pressure just prior to use. Methanol and other solvents were spectroscopic grade. Unless otherwise mentioned all the solutions were deaerated by several freeze—pump—thaw cycles.

Steady state photolysis of methanolic 0.1 M solutions of DMA and various amounts of chlorobenzene was 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 filtered with an alkaline potassium chromate solution.

Chloride ion produced by photolysis was measured with an Orion specific ion electrode. The conversion of halobenzenes was always kept below 5%.

Actinometry was performed with a solution of valerophenone in benzene. A quantum yield of 0.33, independent of temperature, was taken for the production of acetophenone [6]. The hydrogen chloride production from the DMA-sensitized decomposition of chlorobenzene was in good agreement with data reported in the literature [3]. The sensitized decomposition of chlorobenzene was used as an actinometer for the decomposition of the dichlorobenzenes.

Fluorescence measurements were performed with an Aminco SPF 125 spectrofluorometer.

The laser flash photolysis system has been described elsewhere [7]. Excitation at 337 nm was accomplished with a nitrogen laser. The DMA concentration was 0.5 M and the concentration of chlorobenzenes was varied in the range 0.004 - 0.03 M. All solutions were deaerated by bubbling through argon or nitrogen. Right angle excitation was employed with cells of optical path 2 mm.

3. Results and discussion

3.1. Fluorescence quenching of N,N-dimethylaniline by chlorobenzenes

When excited at 310 nm DMA shows a fluorescence spectrum with a maximum at 335 nm in cyclohexane and 345 nm in methanol [3]. Halobenzenes quench this fluorescence and a red shift of the emission was observed in cyclohexane [3]. Since no change was detected in the absorption spectrum the shift was ascribed to the formation of an exciplex between the excited DMA and the halobenzene.

In order to confirm the existence of the exciplex we have studied the fluorescence quenching of DMA by chlorobenzene in different solvents. At low chlorobenzene concentrations the Stern–Volmer plots were linear in all cases. The results are shown in Table 1. The bimolecular quenching rate constants k_q were obtained with the assumption of a fluorescence lifetime τ_0 of 2.8 ns in the alcoholic solvents and 2.4 ns in the less polar solvents, these being the values given by Berlman [8] in ethanol and cyclohexane respectively. The value of τ_0 in cyclohexane was also confirmed by Alford et al. [9].

TABLE 1

Fluorescence quenching of N,N-dimethylaniline by monochlorobenzene in various solvents

Solvent	Stern–Volmer constant K_{SV} (M^{-1})	$k_3 \times 10^{-9}$ [a] (M^{-1} s^{-1})
Methanol	8.0 ± 0.3	3.0
Ethanol	7.7 ± 0.3	2.8
Butanol	3.8 ± 0.2	1.4
Dioxane	1.3 ± 0.1	0.6
Benzene	1.0 ± 0.1	0.4

[a] The fluorescence lifetime was taken as 2.8 ns in polar solvents and 2.4 ns in non-polar solvents.

We considered the rate constants in Table 1 to be accurate only to ±10%. Nevertheless, it is clear that there is a decrease in the rate constant with decreasing dielectric constant of the solvent.

Since the k_q values are below the diffusional limit, a simple mechanism which can explain these results is through the formation of an exciplex:

$$^1DMA^* + ClPh \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} {}^1(DMA\cdots ClPh)^* \xrightarrow{k_a} quenching \qquad (1)$$
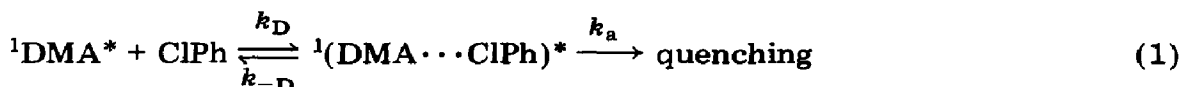
In methanol Pac et al. [3] suggested that a process mediated by an electron transfer exciplex takes place between $^1DMA^*$ and chlorobenzene which we have confirmed as discussed below. From this point of view an increasing contribution to k_a is expected from this electron transfer process with an increase in the dielectric constant.

According to eqn. (1), k_q can be written as

$$k_q = \frac{k_D k_a}{k_{-D} + k_a} \tag{2}$$

An increase in k_a should be reflected as an increase in k_q provided that the ratio k_D/k_{-D} remains essentially unchanged. Therefore we think that the solvent effect on the quenching process confirms the exciplex formation in the less polar solvents.

Also the red shift in the fluorescence band, observed in cyclohexane, is absent in the alcoholic solvents, even at high chlorobenzene concentrations (more than 90% quenching).

We have also studied the effect of a second chlorine atom on the aromatic ring. The results in methanolic solution can be seen in Table 2. In all cases the rate constants are diffusion controlled. This was confirmed by temperature effect studies which resulted in apparent activation energies, for this quenching process, in close agreement with the corresponding viscosity parameter. The higher quenching rate constant of dichlorobenzenes relative to monochlorobenzene are in agreement with an electron transfer process because the dichlorobenzenes are more easily reduced than monochlorobenzene [10].

TABLE 2

Fluorescence quenching of N,N-dimethylaniline in methanol by several chlorobenzenes

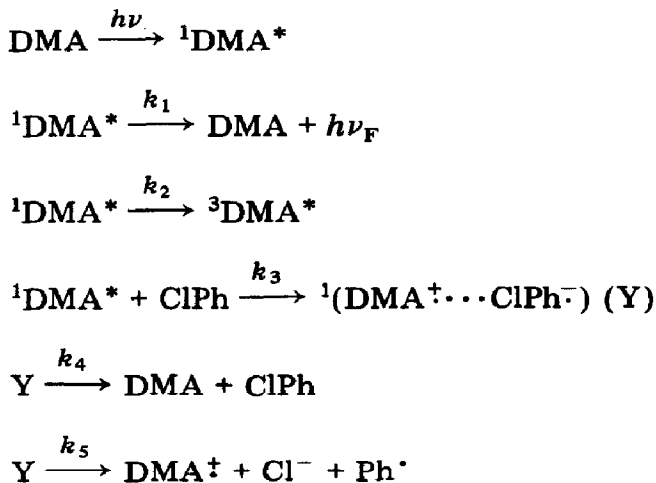| Chlorobenzene	Stern–Volmer constant K_{SV} (M^{-1})	$k_3 \times 10^{-9}$ [a] (M^{-1} s^{-1})
Monochlorobenzene	8 ± 0.3	3
1,2-Dichlorobenzene	33 ± 1.0	12
1,3-Dichlorobenzene	30 ± 1.0	11
1,4-Dichlorobenzene	36 ± 1.0	13
3,4-Dichlorotoluene	28 ± 1.0	10

[a]The fluorescence lifetime was taken as 2.8 ns in methanol.

It was previously reported by Latowski [2] that, when methanolic solutions of DMA are irradiated in the presence of chlorobenzenes, hydrogen chloride is produced with high quantum yields. For a chloro compound concentration of 0.2 M in air-equilibrated solutions, the quantum yields were 0.40 for chlorobenzene, 0.37 for 1,2-dichlorobenzene, 0.53 for 1,3-dichlorobenzene and 0.64 for 1,4-dichlorobenzene. When these results are compared with those from fluorescence quenching, it is readily apparent that there is no simple correlation between both sets of results.

It seems that the photoreaction is not in all cases an electron transfer process mediated by a simple singlet state. Therefore we have undertaken a detailed kinetics study of the photochemical reaction in an attempt to clarify the mechanism.

3.2. Photolysis of N,N-dimethylaniline in the presence of chlorobenzenes

Previous studies [3] have shown that when DMA is irradiated in methanol at 313 nm in the presence of chlorobenzene, hydrogen chloride is produced via the following mechanism.

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

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

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

$${}^1DMA^* + ClPh \xrightarrow{k_3} {}^1(DMA^{\dagger}\cdots ClPh^{\overline{\cdot}}) \; (Y)$$

$$Y \xrightarrow{k_4} DMA + ClPh$$

$$Y \xrightarrow{k_5} DMA^{\dagger} + Cl^- + Ph^{\cdot}$$

Scheme 1.

A steady state analysis of the reaction scheme leads to the following expressions.

$$\Phi_{HCl}{}^{-1} = \frac{1}{\varphi_S} \left\{ 1 + \frac{1}{k_3\tau_0(ClPh)} \right\} \tag{3}$$

where $\tau_0 = (k_1 + k_2)^{-1}$ and

$$\varphi_S = \frac{k_5}{k_4 + k_5} \tag{4}$$

Accordingly, plots of the inverse of the hydrogen chloride quantum yield *versus* the inverse of the concentration of chlorobenzene should be straight lines with slopes and intercepts from which the products $k_3\tau_0$ and k_4/k_5 can be obtained.

In the case of monochlorobenzene we have studied the temperature dependence of the photoreaction in the range 8 - 40 °C. Both the slope and the intercept are temperature independent within the experimental error and in close correspondence with the nearly temperature-independent Stern–Volmer plots obtained by fluorescence quenching experiments. From the inverse plots a value of $k_3\tau_0 = 10 \pm 1$ M^{-1} and $k_4/k_5 = 1 \pm 0.1$ were obtained. They are nearly the same as those of Pac *et al.* [3] at room temperature. When $k_3\tau_0$ is compared with the fluorescence quenching results the similarity with K_{SV} (Table 1) is strong evidence supporting the mechanism in Scheme 1.

At this point it is interesting to comment on the efficiency φ_S of formation of free ions in the electron transfer process. An efficiency of 0.5 as

found in this case seems to be large, in view of the very fast cage recombination expected for a singlet ion pair, initially formed in the same solvent cage [11].

This is probably due to a very fast decomposition of the hypothetically formed chlorobenzene anion radical. In pulse radiolysis studies the anion could not be detected [12] and theoretical work explains its instability [13] by the assignment of a σ^* electronic state to it. Moreover, the temperature independence of k_4/k_5 is also in support of this very fast decomposition of $ClPh^-$.

When DMA is irradiated in the presence of dichlorobenzenes there is no longer a correlation between the fluorescence quenching and the inverse plots of the photolysis studies.

A plot of Φ_{HCl}^{-1} *versus* the inverse of the 1,2-dichlorobenzene concentration under various experimental conditions is shown in Fig. 1. This also shows the hypothetical curve for a mechanism similar to that in Scheme 1 calculated using the Stern–Volmer constant obtained in the fluorescence quenching for $k_3\tau_0$ (Fig. 1, curve c). It can be seen that in deaerated solutions the hydrogen chloride yield (Fig. 1, curve a) is substantially larger than that expected from an electron transfer process from the excited singlet state of DMA (Fig. 1, curve c). This difference leads us to suppose that there is another pathway for hydrogen chloride production, not contemplated in Scheme 1.
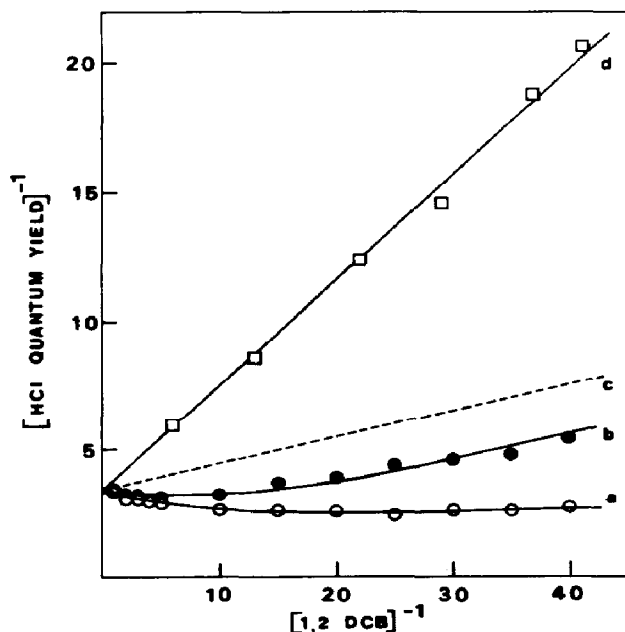

Fig. 1. Plot of the inverse of the hydrogen chloride quantum yield *vs.* the inverse of the 1,2-dichlorobenzene concentration: $\bigcirc$, deaerated solutions; $\bullet$, non-deaerated solutions; $\square$, deaerated solutions with the addition of 0.1 M biphenyl; – – –, theoretical plot if only the DMA singlet state were the sensitizer.

The possibility that this extra process originates in the triplet state of DMA was explored. Thus, when the photolysis of non-degassed solutions was carried out, an inhibition of hydrogen chloride production was observed (Fig. 1, curve b). If all the triplets were quenched by oxygen a straight line should be expected. However, the low oxygen concentration in air-equilibrated solutions is not enough to quench all DMA triplets, as a result of the short lifetime of the DMA triplets in methanolic solutions [14].

The effect of other triplet quenchers was investigated. However, at the necessary concentrations for total DMA triplet quenching, an appreciable amount of DMA singlet quenching was found.

We have determined that biphenyl quenches the fluorescence of DMA with a Stern–Volmer constant of 30.5 ± 0.9 M^{-1} in methanol. It was previously reported that biphenyl also quenches the DMA triplets with a diffusional rate constant [15].

Under conditions of total triplet quenching (concentration of biphenyl, 0.1 M) an extra second-order decay route for the singlet should be added to Scheme 1:

$$^1DMA^* + Bi \xrightarrow{k_6} DMA + {}^3Bi^*$$
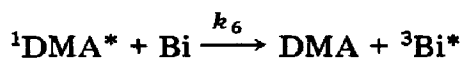
where Bi ≡ biphenyl.

The DMA singlet state lifetime is then

$$\tau^{-1} = \tau_0^{-1} + k_6(Bi) \tag{5}$$

and for the hydrogen chloride yield eqn. (3) should be obeyed with a value of the singlet state lifetime of DMA given by eqn. (5).

The results in the presence of 0.1 M biphenyl can be seen in Fig. 1, curve d. Under these conditions only the singlet reaction should be observed. From the plot in Fig. 1, curve d, using eqns. (3) and (5), a value of $k_3\tau_0$ could be obtained as 34 ± 8 M^{-1} in good agreement with the value in Table 2 for the quenching of DMA fluorescence by 1,2-dichlorobenzene.

It is interesting to note that, in Fig. 1, all the plots have a common origin independent of the experimental conditions. This rules out the possibility that the excess hydrogen chloride yield compared with that expected from a mechanism such as that in Scheme 1 should be due to a chain mechanism similar to that established for SRN_1 reactions [13]. If this were the case a decrease in the hydrogen chloride quantum yield at the origin should be expected in non-deaerated solutions, due to the radical-chain inhibitor character of oxygen.

The most reasonable supposition then is the reaction of the triplet state of DMA with the chlorobenzene. This was suggested by Bunce and Gallacher [4] in the case of the DMA-sensitized photodecomposition of polychlorinated biphenyls.

Another important feature of the plots in Fig. 1 is the minimum observed in deaerated solutions. This is due, as will be shown later, to the fact that at the highest dichlorobenzene concentration a significant fraction

of ^{1}DMA is quenched by the dichlorobenzene and is hence unavailable to form the triplet state.

3.3. *Laser flash photolysis of N,N-dimethylaniline in the presence of chlorobenzenes*

At 337 nm the absorption of DMA in methanol is sufficiently high to observe a strong transient absorption after the nitrogen laser pulse (Fig. 2).

The absorption appearing immediately after the flash with a maximum around 460 nm can be ascribed to both the triplet and the radical cation of DMA [14]. The triplet lifetime under these conditions is around 600 ns; therefore the absorption remaining after 3 μs corresponds to the radical cation.

The intersystem crossing yield was estimated by laser flash experiments with a diluted (10^{-4} M) solution of DMA in methanol with excitation at 266 nm as described elsewhere [14]. Under these conditions the initial absorbance at 460 nm is due mainly to ^{3}DMA*.

The product $\Phi_{isc}\epsilon_T$ was obtained as 3400 ± 300 M^{-1} cm^{-1} with naphthalene in cyclohexane as an actinometer [14]. With a value of 4000 M^{-1} cm^{-1} for the extinction coefficient of triplet DMA, assumed to be the same as that in cyclohexane solution [14], a quantum yield of 0.85 ± 0.1 can be assigned to the intersystem crossing.

The effect of added 1,2-dichlorobenzene on the transient absorption of DMA can also be seen in Fig. 2.

Immediately after the pulse there is less absorption in the presence of the halo compound. This is due to the singlet quenching and there is a good correlation between the change in absorption and the fluorescence quenching experiments.
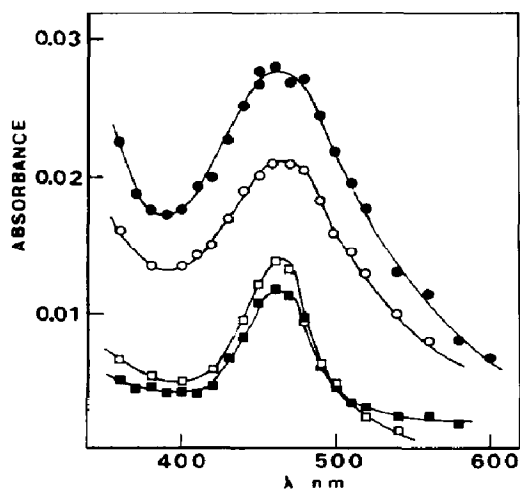

Fig. 2. Transient spectra of 0.5 M DMA in methanol: ●, 200 ns after the flash; ■, 3 μs after the flash; ○, 200 ns after the flash in the presence of 0.013 M 1,2-dichlorobenzene; □, 3 μs after the flash in the presence of 0.013 M 1,2-dichlorobenzene.

However, 3 μs after the flash the absorption is augmented with respect to that in the absence of 1,2-dichlorobenzene, indicating that the DMA cation radical is being formed in larger amounts. It is difficult to evaluate quantitatively the production of the cation radical as a function of the 1,2-dichlorobenzene concentration, since it is already present in the absence of the halobenzene and its yield is probably a complex function of several competitive steps.

In the region around 520 - 540 nm the transient absorption is mostly due to the triplet state, and this fact was employed to measure the DMA triplet state quenching by various chlorobenzenes. The results can be seen in Table 3.

There is a good correlation between the triplet quenching and the photochemical results. Thus, no triplet quenching is observed in the case of monochlorobenzene, in agreement with singlet-state-mediated photochemistry. In the case of 1,2-dichlorobenzene there is appreciable triplet state quenching at the working concentrations in the continuous photolysis experiments, and accordingly the hydrogen chloride yield is larger than that expected from singlet-state-mediated photochemistry.

There are two possibilities for the triplet-sensitized decomposition of dichlorobenzenes: electron transfer and triplet–triplet energy transfer.

The triplet energy of DMA is around 74 kcal mol^{-1} [16] while a value of around 79 - 80 kcal mol^{-1} can be taken for the chlorobenzenes [17]. Then the triplet energy transfer should be slightly endothermic and values such as those in Table 3 for the rate constants of DMA triplet quenching may be possible. However, we believe that this mechanism can be disregarded on the following grounds. First, when we tried to sensitize the decomposition of chlorobenzene with acetophenone (E_T = 74 kcal mol^{-1}) [16], we found an efficiency of less than 5% of that of DMA, in spite of the similarity in the triplet energies. Second, the decomposition of dichlorobenzenes from the triplet states does not seem to be important in methanol. The hydrogen chloride quantum yield plus the intersystem crossing yield is nearly unity for all dichlorobenzenes [18]. Therefore, we believe that the operating mechanism is electron transfer from triplet DMA to

TABLE 3

Quenching rate constants of triplet N,N-dimethylaniline by chlorobenzenes[a]

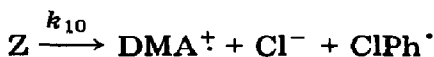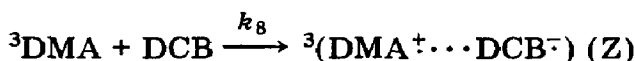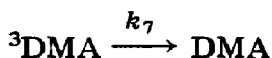| Chlorobenzene	$k_8 \times 10^{-7}$ (M^{-1} s^{-1})
Monochlorobenzene	—
1,2-Dichlorobenzene	8.8 ± 0.6
1,3-Dichlorobenzene	1.9 ± 0.2
1,4-Dichlorobenzene	1.4 ± 0.2
3,4-Dichlorotoluene	21.0 ± 2.0

[a]The lifetime of the DMA triplet state is 560 ± 50 ns.

dichlorobenzene. The free energy change of the electron transfer process can be estimated to be approximately zero from

$$\Delta G^T \approx E_{DMA}{}^{ox} - E_{DCB}{}^{red} - E_{00}{}^T \tag{6}$$

where $E_{DMA}{}^{ox} = 0.81$ eV [19], $E_{DCB}{}^{red} = -2.21$ eV [10] and $E_{00}{}^T = 3.05$ eV [16]. The above result is in reasonable agreement with the observed second-order rate constant of the DMA triplet state quenching by dichlorobenzenes.

3.4. General mechanism for the dechlorination of chlorobenzenes sensitized by N,N-dimethylaniline

In addition to 1,2-dichlorobenzene we also studied the photochemistry of the systems DMA–1,3-dichlorobenzene, DMA–1,4-dichlorobenzene and DMA–3,4-dichlorotoluene. The inverse plots for these three compounds can be seen in Fig. 3. According to the results of triplet quenching presented above, we propose as a general mechanism that shown in Scheme 1 plus the following reactions.

$$^3DMA \xrightarrow{k_7} DMA$$

$$^3DMA + DCB \xrightarrow{k_8} {}^3(DMA^{\ddagger}\cdots DCB^{\bar{}}) \; (Z)$$

$$Z \xrightarrow{k_9} DMA + DCB$$

$$Z \xrightarrow{k_{10}} DMA^{\ddagger} + Cl^- + ClPh^{\cdot}$$

The total hydrogen chloride yield must be the sum of the singlet and triplet electron transfer contributions:

$$\Phi_{HCl}^{total} = \Phi_{HCl}^1 + \Phi_{HCl}^3 \tag{7}$$

A steady state analysis of the full mechanism leads to

$$\Phi_{HCl} = \frac{\varphi_S}{1 + 1/k_3\tau_0^1(DCB)} + \frac{\varphi_T\Phi_{isc}}{\{1 + 1/k_8\tau_0^3(DCB)\}\{1 + k_3\tau_0^1(DCB)\}} \tag{8}$$

where

$$\tau_0^1 = \frac{1}{k_1 + k_2} \tag{9}$$

$$\tau_0^3 = \frac{1}{k_7} \tag{10}$$
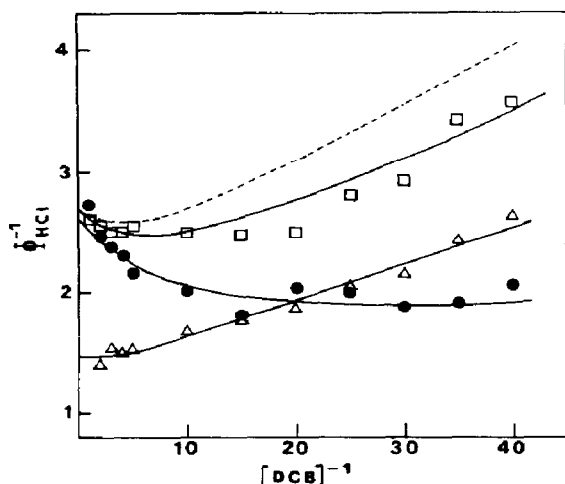
$$\varphi_S = \frac{k_5}{k_4 + k_5} \tag{11}$$

Fig. 3. Plot of the inverse of the hydrogen chloride quantum yield *vs.* the inverse of several dichlorobenzene concentrations: △, 1,4-dichlorobenzene; ●, 3,4-dichlorotoluene; ▫, 1,3-dichlorobenzene; – – –, hypothetical plot if the efficiency of the triplet DMA–1,3-dichlorobenzene radical pair to give hydrogen chloride were 0.8.

$$\varphi_T = \frac{k_{10}}{k_9 + k_{10}} \tag{12}$$

In eqn. (8), the products $k_3\tau_0^1$ and $k_8\tau_0^3$, the Stern–Volmer constants for singlet and triplet quenching respectively, can be replaced by the experimental results obtained in fluorescence quenching and laser flash photolysis experiments. The intersystem crossing quantum yield is taken as 0.85. φ_S can be obtained from the inverse plots by extrapolation to the origin and the only unknown parameter is φ_T.

From a consideration of the already large values of φ_S, and the spin forbidden nature [11] of step (9) compared with step (5), a high efficiency for ion production in the triplet quenching process can be expected.

We have taken the maximum possible value for φ_T, *i.e.* unity, and the theoretical plot of the inverse of the hydrogen chloride quantum yield *versus* the inverse of the concentration of dichlorobenzene was calculated with eqn. (8), which does not contain any adjustable parameters. Figure 1, curve a, was calculated in this way and it can be seen that the agreement with the experimental points is very good.

However, a more objective treatment of the experimental results is to fit them, as shown in Fig. 3, by a least-squares analysis of eqn. (8) where φ_S and φ_T remain as adjustable parameters. Table 4 shows the values of φ_S and φ_T which give the best fit of eqn. (8) to the experimental points.

It can also be seen that φ_T is nearly unity in all the cases studied, and is in good agreement with the supposition of the spin forbidden nature of step (9).

Moreover, the possibility that φ_T is less than unity was explored. An example is shown in Fig. 3 where an arbitrary value of 0.8 was used for φ_T.

TABLE 4

Efficiencies of the singlet and triplet N,N-dimethylaniline–chlorobenzene radical pair to give hydrogen chloride

Chlorobenzene	φ_S	φ_T
Monochlorobenzene	0.50 ± 0.02	—
1,2-Dichlorobenzene	0.29 ± 0.01	0.94 ± 0.02
1,3-Dichlorobenzene	0.37 ± 0.01	0.98 ± 0.08
1,4-Dichlorobenzene	0.68 ± 0.02	0.97 ± 0.10
3,4-Dichlorotoluene	0.38 ± 0.02	0.99 ± 0.04

In this case the fitting of eqn. (8) to the experimental points is not good over all the concentration range. This fact was found to be general and we can assert that φ_T can be given a value of unity with an error margin of less than 10%.

It is important to note that φ_T is approximately unity in all cases in spite of the large difference in the values of k_8 (Table 3). This fact, we think, is another proof of the consistency of the general mechanism.

With regard to the different triplet quenching abilities of chlorobenzenes, the observed trend can be related to the electron acceptor capabilities of the compounds. Thus monochlorobenzene, which is less easily reduced [10] than dichlorobenzenes, is inefficient towards the triplet of DMA. Nevertheless, the observed difference among the dichloro compounds (Table 3) cannot be explained in terms of the redox potentials which are approximately the same for all these compounds [10] and the difference probably arises from some steric restraint in step (8).

In summary, we have shown that the DMA-sensitized decomposition of chlorobenzenes occurs through a mechanism which involves electron transfer from both the singlet and the triplet state of DMA to the chloro compounds. The relative importance of the singlet and triplet state reactions depends on the reduction potential and the substitution pattern of the chlorine atoms in the chlorobenzene.

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