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LASER FLASH PHOTOLYSIS OF CHLOROBENZENE IN POLAR SOLVENTS

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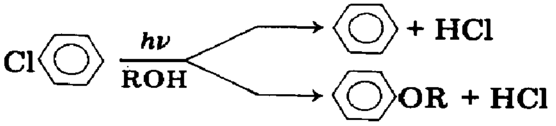
Summary

The laser flash photolysis of chlorobenzene at 266 nm was studied in methanol (MeOH) and other polar solvents. The triplet state properties in MeOH were determined: $\phi^T = 0.7 \pm 0.2$; $\lambda_{max} = 305$ nm; $\epsilon_{305} = 6500 \pm 800$ M^{-1} cm^{-1}; $\tau = 715 \pm 20$ ns. In the presence of LiCl a long-lived transient absorption with $\lambda_{max} = 350$ nm was observed and it was assigned to $Cl_2^{\cdot -}$. Part of the absorption was formed immediately after the laser pulse and a slow growth was also observed in the following microsecond. This was interpreted as being partly due to a singlet state very fast C—Cl bond homolysis and partly due to a triplet-mediated generation of Cl·. Also the characteristic absorption of solvated electrons was found in MeOH. A photo-ionization quantum yield of 0.03 ± 0.01 was estimated. The triplet lifetime was determined in various solvents and it was found to decrease with increasing dielectric constant. The photolysis mechanism of chlorobenzene is discussed in terms of a singlet state photosubstitution reaction with the radical cation as an intermediate, and a singlet and triplet homolytic C—Cl bond breakage.

1. Introduction

The photochemical behavior of chlorobenzene (ClPh) irradiated at 254 nm is affected by the type of solvent. In cyclohexane the main initial process is photoreduction to benzene and the photodecomposition quantum yield has been reported to be in the range 0.3 - 0.4 [1 - 4]. However in hydroxylic solvents photoreduction (reaction (1)) and photosubstitution (reaction (2)) by the solvent occur simultaneously [5 - 7]:



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The total dechlorination quantum yield ϕ_{HCl} was found to be 0.14 in methanol (MeOH) [8] and the ratio of reactions (1) and (2) measured as [benzene]/[anisole] was reported as 4.1 [6]. In H_2O–EtOH (Et ≡ ethyl) mixtures the products are benzene, phenol and phenetole [7] and the quantum yield of dechlorination depends on the solvent composition, with values between 0.1 and 0.27 [7]. The ratio of the photosubstitution products, [phenol]/[phenetole], changes with the solvent composition and is directly proportional to the molar ratio of H_2O to EtOH. This suggests that the precursor of this product must be a very reactive intermediate which does not discriminate between H_2O and EtOH. It has been proposed [7] that the phenyl cation or chlorobenzene radical cation could be this intermediate. In MeOH the photosubstitution was explained by an electron transfer reaction of the excited triplet with ground state ClPh [6], and a subsequent nucleophilic attack by the solvent on the radical cation.

The multiplicity of the excited states and the detailed mechanisms of these photoprocesses have not been clearly established. The phenyl—Cl bond homolysis from the triplet was suggested as the primary step in cyclohexane [3, 4] while the excited singlet was proposed for the homolysis in methanol [6]. For the photosubstitution the excited singlet was considered to be the precursor of the reaction, because of the lack of quenching by oxygen [7]. However acetone sensitization experiments [6] were used to suggest the triplet state mechanism.

We think that part of this controversy can be solved by the direct observation of the intermediates generated by laser flash excitation of ClPh. The first application of the laser flash technique to ClPh was by Lindqvist *et al.* [9]. They determined the triplet–triplet absorption spectrum in cyclohexane and the first-order decay rate constant in cyclohexane and in MeOH. The values were 2.1×10^6 s^{-1} and 2.4×10^6 s^{-1} respectively. Subsequently we redetermined the photophysical parameters in cyclohexane and found that a triplet–triplet annihilation process takes place. The rate constant for decay, extrapolated to zero triplet concentration, was $(6.1 \pm 0.3) \times 10^5$ s^{-1} [10]. In this paper we present a study of the laser flash photolysis at 266 nm in other solvents in order to clarify some aspects of the photophysical and photochemical properties of ClPh.

2. Experimental details

ClPh (Baker analyzed) was further purified by fractional distillation. The solvents were of the highest purity commercially available (spectrophotometric grade) and were used without further purification. LiCl and anthracene (Aldrich, Gold Label) were used as received.

The computer-controlled laser flash photolysis system has been described elsewhere [11]. Excitation at 266 nm was accomplished with an Nd–YAG laser (Quanta Ray) with frequency quadruplication. The laser pulse width was 6 ns. The excitation beam was defocused over the ground face of 2 mm or 10 mm absorption cells in order to eliminate hot spots in the beam. The excitation was at 90° with respect to the analyzing beam. A photodiode was employed in conjunction with a beam splitter to measure the laser intensity. All the solutions were deaerated by purging with oxygen-free nitrogen or argon.

3. Results

When ClPh is irradiated at 266 nm in MeOH the transients observed depend on the laser intensity. At low intensity the only strong absorption is that of the triplet state with a spectrum similar to that in cyclohexane [10] ($\lambda_{max} = 305$ nm). At high laser intensity a second absorption with a very short lifetime (less than 100 ns) appears in the region beyond 400 nm. The complete spectrum under these conditions can be seen in Fig. 1. The broad absorption band with a maximum at about 640 nm coincides with the absorption spectrum of solvated electrons in MeOH [12]. Moreover this absorption is suppressed by saturation with N_2O. Therefore it can be concluded that ClPh undergoes a photo-ionization process under these conditions. Figure 1 also shows the dependence of the absorptions at 305 and 640 nm on laser intensity. The curvature of the plots is indicative of a biphotonic process operating in the system. However from a plot of the logarithm of the optical density *versus* the logarithm of the intensity at 640 nm a slope of 1.5 is obtained. This indicates that the process is not purely biphotonic and that a monophotonic component can be estimated from the initial slope in the plot of the inset in Fig. 1. From the negative curvature of the plot for the triplet (305 nm) it cannot be concluded whether the state involved in the biphotonic process is the triplet itself or the excited singlet. In any case, the curvature cannot be due to ground state depopulation, because

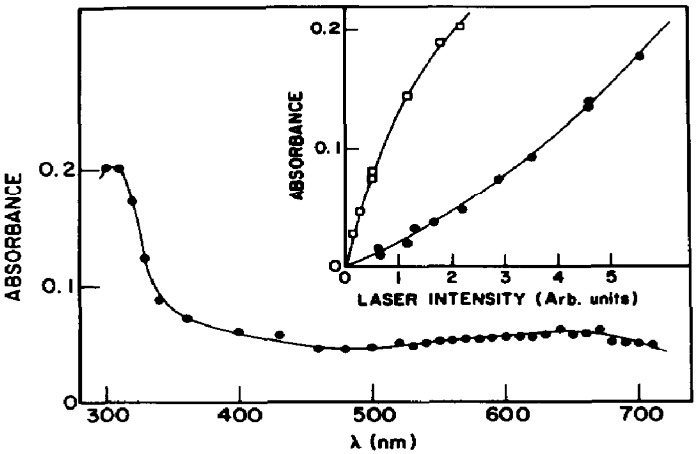

Fig. 1. Transient absorption spectrum of 0.004 M ClPh in MeOH at high laser intensity and immediately after the laser pulse. Inset: end-of-pulse absorbance at 305 nm (□) and 640 nm (●) as a function of the laser intensity.

of the low extinction coefficient of ClPh at 266 nm. Also it is indicative that a two-step biphotonic process occurs and that we are not observing a two-photon absorption by ground state ClPh.

3.1. Triplet state properties in methanol

The triplet decays by a first-order process that is independent of ClPh concentration and of laser intensity. There is some remaining absorption (about 5% of the maximum) at 305 nm which is probably due to a long-lived radical formed by secondary reactions. The lifetime is 715 ± 20 ns (very much shorter than that in cyclohexane [10] (1.6 μs)). Also the triplet–triplet annihilation process found in cyclohexane was not present in MeOH, probably owing to the shorter lifetime.

From the initial slope for the triplet yield *versus* laser intensity (inset, Fig. 1) the product $\phi^T\epsilon^T$ was determined where ϕ^T is the intersystem crossing quantum yield and ϵ^T is the triplet extinction coefficient at 305 nm. Naphthalene in cyclohexane was used as an actinometer. Solutions of matched absorbances for ClPh and the actinometer were used and the triplet yield of naphthalene was monitored at 414 nm. A triplet quantum yield and extinction coefficient of 0.75 and 24 500 M^{-1} cm^{-1} respectively were employed for naphthalene [13]. In this way a value of 4800 ± 500 M^{-1} cm^{-1} was obtained for $\phi^T\epsilon^T$ of ClPh in MeOH.

The triplet extinction coefficient was estimated by energy transfer to anthracene. Using anthracene concentrations in the range 10^{-4} - 10^{-5} M it was found that most of the light at 266 nm was absorbed by ClPh. The small fraction of direct excitation was measured in blank experiments and was subtracted from the experimental results. The triplet absorption spectrum of anthracene in MeOH was determined. It was similar to that in cyclohexane and EtOH [14], with the sharp maximum occurring at 420 nm. We estimated an extinction coefficient of $(5.5 \pm 0.5) \times 10^4$ M^{-1} cm^{-1} at 420 nm for the anthracene triplet in MeOH using an extinction coefficient of 64 700 M^{-1} cm^{-1} [13] for the same species in cyclohexane. This should be compared with a value of 48 500 M^{-1} cm^{-1} in EtOH [14].

After the laser pulse in the presence of anthracene a growth was observed at 420 nm which matches the decay at 305 nm. From this growth the rate constant for energy transfer was calculated. Its value ($(1.8 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}) coincides with that expected for a diffusion-controlled rate process in MeOH. With this rate constant and the plateau reached at 420 nm, the extinction coefficient of ClPh triplet at 305 nm was estimated by standard procedures [13]. The mean value from several independent measurements at different anthracene concentrations was 6500 ± 800 M^{-1} cm^{-1}.

From this and the actinometric results an intersystem crossing quantum yield of 0.7 ± 0.2 results for ClPh in MeOH. This should be compared with 0.6 ± 0.1 reported in cyclohexane [3, 4]. It can be concluded that the solvent polarity hardly affects the triplet yield, which is in agreement with the results typically found for aromatic molecules [14].

The fluorescence quantum yield was also determined using the same technique as for ClPh in cyclohexane [10]. A value of 0.008 ± 0.002 was obtained, which is also very similar to the value in cyclohexane (0.007) [10].

3.2. Photo-ionization in methanol

Using the same method as for the triplet actinometry we determined the product $\phi_e \epsilon_e$ where ϕ_e is the photo-ionization quantum yield and ϵ_e is the extinction coefficient of the solvated electrons in MeOH. A value of 400 ± 100 was obtained by extrapolation to zero laser intensity. From this and by using the value 16 000 M^{-1} cm^{-1} [15] for ϵ_e, a quantum yield of 0.03 ± 0.01 is obtained for the monophotonic photo-ionization.

The electron decays with a lifetime of less than 100 ns. The rate of decay does not follow a simple kinetic law. It increases with the electron and ClPh concentrations, but it cannot be explained by simple homogeneous kinetics. This behavior is similar to that found by Grossweiner *et al.* [16] for the decay of the electron photogenerated in H_2O and is also similar to our results for the photo-ionization of other aromatic compounds in alcohols [17].

3.3. Effect of added LiCl

On the assumption that the primary photolytic act leading to the photoreduction process (reaction (1)) was the homolytic splitting of the C—Cl bond, we tried to trap the chlorine atoms as $Cl_2^{-\cdot}$ by means of a high concentration of LiCl. The transient absorption spectra, at low laser intensity in the presence of 4.0 M LiCl, can be seen in Fig. 2. The figure also shows for the sake of comparison the corresponding transient spectra in the absence of LiCl. At 3 μs after the laser pulse a new spectrum appears in the presence of LiCl. This absorption is very similar to that of $Cl_2^{-\cdot}$ in H_2O

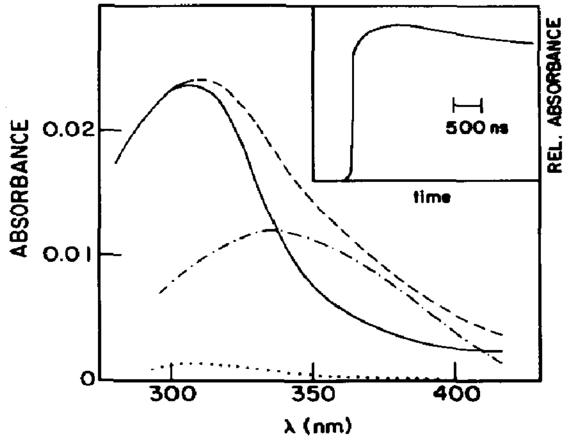

Fig. 2. Transient absorption spectrum of 0.008 M ClPh in MeOH: ——, immediately after the flash; · · ·, 3 μs after the flash; — — —, in the presence of 4.0 M LiCl immediately after the flash; — · —, in the presence of 4.0 M LiCl 3 μs after the flash. Inset: time profile of the absorption at 360 nm in the presence of 4.0 M LiCl.

[18] except that it is shifted to the blue by about 10 nm. But the main feature in the spectral changes is observed immediately after the laser pulse. It can be seen that $Cl_2^{-\cdot}$ is present initially and this causes the increased absorption in the region around 350 nm. Also the inset in Fig. 2 shows the time profile of the absorption at 360 nm in the presence of LiCl. The growth observed after the initial jump indicates that there is a second slower process by which $Cl_2^{-\cdot}$ is being formed. We do not believe that it is possible to evaluate quantitatively these observations in terms of quantum yields for the following reasons. Firstly, there is most probably a competition for reaction with chlorine atoms between Cl^- and the solvent; the reaction $Cl\cdot + Cl^-$ in H_2O is known to be diffusion controlled [18], but to our knowledge a value for the rate constant for $Cl\cdot$ + MeOH in the liquid phase is not available in the literature. Secondly, the extinction coefficient of $Cl_2^{-\cdot}$ in MeOH has not been determined.

3.4. Solvent effect on the triplet lifetime

The effect of other polar solvents on the triplet lifetime τ can be seen in Fig. 3 in which τ is plotted against dielectric constant. The decay follows a simple first-order law in all solvents and the triplet–triplet absorption spectrum shows only minor changes on going from cyclohexane to H_2O. In all cases the maximum is around 300 nm. It is interesting to note that while most solvents employed are of the hydroxylic type the values for cyclohexane and acetonitrile lie on the same curve, so we believe that the observed effect is a general one related to the polarity of the medium and not to a specific interaction with a certain type of solvent.

The low value for the triplet lifetime in H_2O was also observed by Treinin and Hayon [19], who were also unable to observe the formation of $Cl_2^{-\cdot}$ on addition of KCl. This confirms our previous result [7] that homolytic bond splitting is a minor process in H_2O.

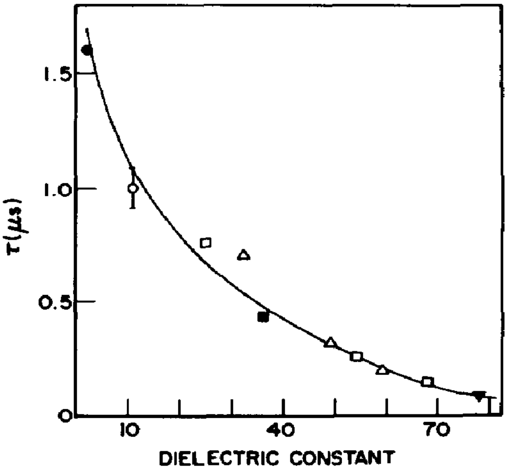

Fig. 3. Triplet lifetime *vs.* dielectric constant: ●, cyclohexane; ○, *t*-butanol (30 °C); □, EtOH and EtOH–H_2O; △, MeOH and MeOH–H_2O; ■, acetonitrile; ▼, H_2O.

4. Discussion

As was pointed out in the Introduction the two main photoprocesses of ClPh in hydroxylic solvents are photoreduction and nucleophilic photosubstitution by the solvent. The latter process was thought to occur through the attack on the solvent by some positive species originating from the excited singlet state of ClPh [7]. From the photodechlorination quantum yield in MeOH ($\phi_{HCl} = 0.14$ [8]) and from the ratio [benzene]:[anisole] in the same solvent (4.1 [5]) and assuming

$$\phi_{HCl} = \phi_{benzene} + \phi_{anisole} = \phi_R + \phi_S \qquad (3)$$

where ϕ_R and ϕ_S are the quantum yields for reaction (1) and reaction (2) respectively, the absolute values $\phi_R = 0.11$ and $\phi_S = 0.03$ can be estimated. The validity of a mass balance equation such as eqn. (3) was established for the photolysis in EtOH–H_2O mixtures [7].

If ϕ_S is compared with the quantum yield of photo-ionization found in this work (0.03 ± 0.01) it can be concluded that the reaction intermediate is most probably the radical cation.

Considering the results in the presence of LiCl, the following mechanism can be written for the photolysis in MeOH:

$$\mathrm{ClPh} \xrightarrow{h\nu} {}^1\mathrm{ClPh}^* \qquad (4)$$

$${}^1\mathrm{ClPh}^* \longrightarrow \mathrm{ClPh} + \text{fluorescence} + \text{heat} \qquad (5)$$

$${}^1\mathrm{ClPh}^* \longrightarrow \mathrm{Cl}\cdot + \mathrm{Ph}\cdot \qquad (6)$$

$${}^1\mathrm{ClPh}^* \longrightarrow {}^3\mathrm{ClPh}^* \qquad (7)$$

$${}^1\mathrm{ClPh}^* \longrightarrow \mathrm{ClPh}^{+\cdot} + e_S \qquad (8)$$

$$\mathrm{ClPh}^{+\cdot} \xrightarrow{\mathrm{ROH}} \mathrm{PhOR} + \mathrm{H}^+ + \mathrm{Cl}\cdot \qquad (9)$$

$${}^3\mathrm{ClPh}^* \longrightarrow \mathrm{ClPh} \qquad (10)$$

$${}^3\mathrm{ClPh}^* \longrightarrow \mathrm{Cl}\cdot + \mathrm{Ph}\cdot \qquad (11)$$

and in the presence of LiCl

$$\mathrm{Cl}\cdot + \mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2^{-\cdot} \qquad (12)$$

where ^{1}ClPh* and ^{3}ClPh* represent the excited singlet and excited triplet respectively.

We did not observe any concentration effect on the triplet lifetime in the range 0.004 - 0.02 M. So, the electron transfer reaction between triplet and ground state ClPh:

$$^{3}\mathrm{ClPh}^{*} + \mathrm{ClPh} \longrightarrow \mathrm{ClPh}^{\cdot+} + \mathrm{ClPh}^{-}$$

which was proposed by Soumillion and DeWolf [6] can be disregarded.

From the observed spectrum and time evolution at 360 nm in the presence of 4.0 M LiCl (Fig. 2) we can establish reactions (6) and (11) as the homolytic bond splitting processes. At the high concentration of Cl^- employed, assuming a diffusion-controlled rate constant for reaction (12), all chlorine atoms will react in less than 1 ns with either Cl^- or the solvent. The absorbance around 350 nm immediately after the laser pulse (in the time scale of our experiments, less than 40 ns) is increased in the presence of LiCl. This can be explained by a very fast formation of $Cl\cdot$ (reaction (6)). A small growth is also observed during the next microsecond and we think that this is due to a second slower generation of $Cl\cdot$ (reaction (11)). Reaction (9) is another source of $Cl\cdot$, but we believe that this is a very fast process which contributes only to a fraction of the initial $Cl\cdot$. Since the triplet lifetime is not affected by the presence of the salt we can disregard a direct reaction of the triplet with Cl^-.

In Table 1 we have collected the quantum yields for reactions (1) and (2) obtained by continuous photolysis and the triplet lifetimes obtained in this work. It can be seen that the photoreduction decreases as the lifetime decreases. This suggests that the rate of reaction [10] increases with solvent polarity, *i.e.* the effect shown in Fig. 3 is due to a faster non-reactive decay as the polarity of the solvent increases. This decay route is probably favored by the higher dipolar nature of the excited state compared with the ground state, and subsequent interaction with the polar solvent molecules.

In a previous work [7] the quenching effect of oxygen on the photoreaction was explained assuming that the homolytic process originates entirely in the triplet state. In this way triplet lifetimes were estimated which

TABLE 1

Photolysis quantum yields and triplet lifetimes in different solvents

Solvent	ϕ_{HCl}	ϕ_R	ϕ_S	τ (ns)
Cyclohexane	—	0.4[a]	—	1600[b]
Methanol	0.14[c]	0.11[d]	0.03[d]	720[e]
$EtOH-H_2O$ (1:1)	0.20[f]	0.14[f]	0.04[f]	260[e]
$EtOH-H_2O$ (1:3)	0.13[f]	0.08[f]	0.06[f]	140[e]
H_2O	0.10[f]	0.01[f]	0.06[f]	70[e]

[a] From refs. 3 and 4.
[b] From ref. 10.
[c] From ref. 8.
[d] From refs. 6 and 8 and eqn. (3).
[e] This work.
[f] From ref. 7.

are very much lower than the actual values. This discrepancy is probably due to a considerable fraction of the homolysis arising from the very short-lived singlet state and not being quenched by oxygen.

In summary, we have presented evidence which indicates that in polar solvents the process of C—Cl bond breakage takes place from both the excited singlet state and the triplet state. Also the observed photo-ionization of ClPh in MeOH suggests that the photosubstitution by the solvent occurs via the radical cation.

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