

PHOTOCHEMISTRY OF CHLOROBENZENE IN ETHANOL-WATER SOLUTIONS

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Summary

Chlorobenzene was irradiated at 254 nm in ethanol-water mixtures. The main products were HCl, benzene, phenol and phenetole. Quantum yields were obtained in degassed solutions and under different pressures of oxygen.

The results were interpreted in terms of a photosubstitution reaction from the singlet state, which involves electrophilic attack to the solvent by a very reactive intermediate. Simultaneously a homolytic bond rupture in the triplet state takes place, which increases with decreasing solvent polarity.

1. Introduction

The photochemistry of aryl halides has been very actively investigated in recent years. The subject is of current interest because of its relevance to the photoinduced degradation of chlorinated hydrocarbons, widely used as pesticides, and to the potential application in organic synthesis [1]. From the point of view of the ambient photodegradation of chlorinated aromatic compounds, the results are of special interest when obtained in aqueous media; however, most studies on the photochemistry of these compounds have been carried out in organic solvents.

Photolysis of aryl halides is well known to lead to the homolytic fission of the carbon-halogen bond in non-polar solvents [2]. However, in aqueous or alcoholic media a photosolvolytic reaction takes place [1, 2].

Kulis *et al.* [3] studied the photolysis of benzene and pyridine halo derivatives in various media. They found that chlorobenzene irradiated at 254 nm in aqueous solutions (13% EtOH) afforded phenol with a quantum yield of 0.08. In methanol as solvent they reported the formation of benzene as the reaction product (quantum yield, 0.02). However, Latowska and Latowski [4] measured a quantum yield of 0.14 for HCl in methanol. This discrepancy can be attributed in part to the formation of anisole, which was not considered by these researchers and afterwards was detected in this sys-

tem [5]. These results were interpreted [3, 5] as arising from a homolytic or a heterolytic photoreaction, depending on the nature of the solvent.

With regard to the multiplicity of the excited states and the nature of the intermediates responsible for these processes, different and contradictory views were sustained. Thus, in the photosolvolysis the formation of a pair of radical ions via a triplet excimer was proposed as a key step in the mechanism [5]. However, the singlet excited state of chlorobenzene was proposed for the photohydrolysis [3].

With respect to the homolytic photoreduction, the triplet state was suggested for chlorobenzene in cyclohexane [6], whereas in methanolic solutions the excited singlet state is assumed to have a prominent role [5].

In view of these contrasting opinions we decided to study the photochemistry of chlorobenzene in EtOH-H₂O mixtures, where both processes take place. In the previous work mentioned above either the disappearance of chlorobenzene or the appearance of one product of the reaction was generally monitored. In this work we present results on the quantum yields of all the main products of the photolysis of chlorobenzene in these media, and how they are affected by different experimental conditions. These results may be interpreted in terms of a mechanism which involves a triplet state homolytic photoreduction and a singlet state heterolytic photosubstitution by the solvent.

2. Experimental details

2.1. Materials

Chlorobenzene (Fluka) was purified by fractional distillation and its purity was checked by gas-liquid chromatography. Triply distilled water was used throughout. EtOH was doubly distilled and its purity was checked by UV absorption and fluorescence. Benzene, phenol and phenetole, used as standards for the gas chromatography, were commercially available and were used without further purification.

2.2. Photochemical procedures

Chlorobenzene was dissolved in EtOH-H₂O mixtures. Its concentration ranged from 10^{-3} to 2×10^{-2} M in the mixtures. The absorbances of the solutions were determined at 254 nm and degassing was accomplished by freeze-thaw cycles in a vacuum line. In the experiments with added oxygen the gas was equilibrated over the solutions in the vacuum line and the pressure was determined manometrically before the ampoules were sealed. The oxygen concentration for the different EtOH-H₂O mixtures was estimated by standard procedures [7] from the solubility data in pure water and EtOH. Up to eight samples of 5 ml each were irradiated at 25 ± 0.5 °C in a merry-go-round photoreactor equipped with UV lamps (General Electric FG 8132A; 15 W).

2.3. Products analysis

HCl was determined as chloride ion with a specific electrode (Orion 92-17A) in a 701 Orion pH meter. Chlorobenzene, benzene, phenol and phenetole were measured by gas chromatography on a Varian 2828 equipped with a 1/8 in \times 5 ft column packed with Porapak Q. Phenol was also determined by adding a few drops of KOH to the photolysed solutions and reading the absorbance of the phenolate anion.

Actinometry was provided by simultaneous irradiation of monochloroacetic acid. A quantum yield of 0.32 at 25 °C was taken for the production of chloride ion [8].

3. Results

When chlorobenzene solutions are photolysed at 254 nm in EtOH-H₂O mixtures, HCl, phenol, phenetole and benzene are formed. The quantum yields in degassed conditions are given in Table 1. Within the estimated experimental error (about 10%) a reasonable agreement between the quantum yield for HCl and the sum of the quantum yields for phenol, phenetole and benzene is found. The slight deficiency in the sum of the quantum yields of the organic compounds can be attributed to the presence of other minor products. One of these was identified as biphenyl and it amounts approximately to 2% of the benzene produced.

TABLE 1

Quantum yields for the photolysis of chlorobenzene at 254 nm

Solvent	EtOH:H ₂ O molar ratio	Quantum yields ^a for the following products			
		HCl ^b	Phenol ^c	Benzene ^c	Phenetole ^c
H ₂ O	—	0.10	0.062	0.010	—
H ₂ O-25%EtOH	0.099	0.13	0.051	0.078	0.006
H ₂ O-50%EtOH	0.290	0.20	0.026	0.14	0.010
H ₂ O-75%EtOH	0.820	0.27	0.022	0.19	0.019

^a 25 °C; degassed solutions; mean values of several runs.

^b Conversion less than 5%; estimated error, \pm 5%.

^c Conversion up to 20%; estimated error, \pm 10%.

3.1. Effects of added KOH

To check whether phenol could arise from a reaction with OH⁻, photolyses were carried out in the presence of various concentrations of KOH, in the range 0.005 - 0.5 M in pure water. The quantum yields were the same as those in neutral solutions.

3.2. Effect of oxygen

Photolyses were also performed in air-saturated solutions and at various pressures of oxygen. Under these conditions the phenol and phenetole quan-

tum yields were the same as those for degassed solutions. In contrast, the quantum yield for HCl was lowered. The yield of benzene was also affected by oxygen but, since it is produced in smaller quantities than HCl, it was not possible to obtain precise results for its dependence on oxygen.

3.3. Effect of concentration

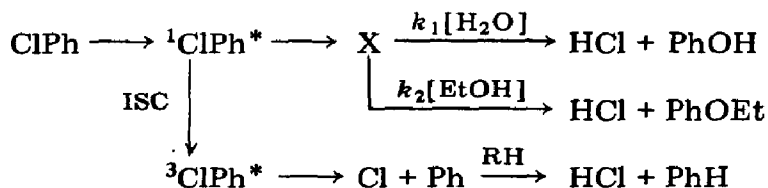
The chlorobenzene concentration was varied by at least a factor of 2 and in some solvent mixtures by a factor of 4. The quantum yields for the production of HCl remained unchanged in all cases.

4. Discussion

It is well documented that in alkane solvents aryl halides undergo an efficient photoreduction with production of the corresponding arene and HCl [1, 6]. In nucleophilic solvents such as alcohols photosubstitution and photoreduction occur simultaneously [5]. From our results in Table 1 it can be seen that both processes occur simultaneously even in pure water, when it may be expected that photoreduction would be suppressed. The relative amount of the reduction products increased with increasing concentration of EtOH as expected.

The ratio of the products of the photosubstitution reaction, phenol and phenetole, changes with the solvent composition, but the sum of the quantum yields does not show a great variation in going from pure water (0.062) to the solvent richest in EtOH (0.041). The quantum yields are also unaffected by the presence of dissolved oxygen. These results suggest that these products arise from a very reactive intermediate originating from the excited singlet state of chlorobenzene.

The quenching effect of oxygen on the quantum yields for HCl and benzene suggests that the photoreduction process originates in the triplet state in agreement with findings of other workers for organic solvents [6]. The facts presented to date can be explained in terms of the following reaction scheme:



Here ${}^1\text{ClPh}^*$ represents the excited singlet of chlorobenzene and ${}^3\text{ClPh}^*$ the triplet state, and ISC represents the intersystem crossing between them. X is an intermediate arising from the excited singlet through a heterolytic process. RH represents the solvent which acts as a hydrogen donor.

According to the above scheme the ratio $\phi_{\text{phenetole}}/\phi_{\text{phenol}}$ of the quantum yield for phenetole to that for phenol should be directly related to the EtOH:H₂O molar ratio as is found (Fig. 1).

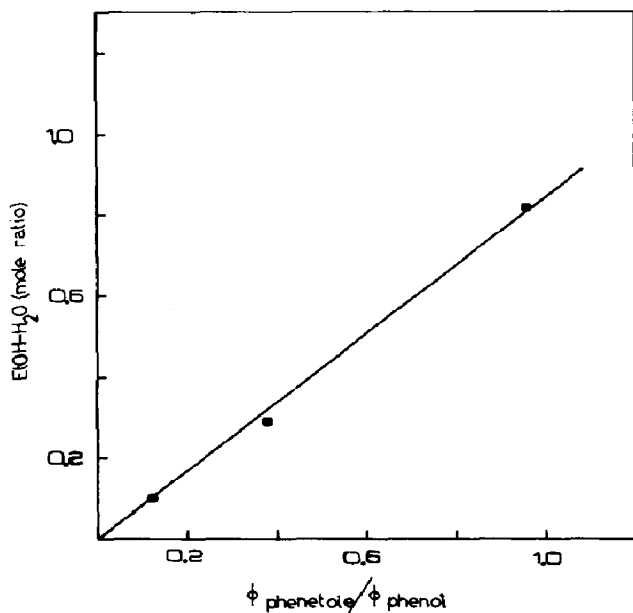


Fig. 1. Effect of the solvent composition on the ratio $\phi_{\text{phenetole}}/\phi_{\text{phenol}}$ of the quantum yields for the photolysis of chlorobenzene at 254 nm.

The absence of any effect on the yield of phenol when KOH is added and the near-unity slope in Fig. 1 suggest that X must be very reactive towards the solvent and that it does not discriminate between water and ethanol. Two possibilities arise for the chemical nature of X: (a) a phenyl cation, originated by a heterolytic bond fission in the excited state



and (b) a chlorobenzene cation radical formed by electron ejection from the excited singlet to the solvent.

A phenyl cation was previously proposed in the photosolvolysis of 3,4-dichloroaniline in water [9]. However, the cation radical was suggested as an intermediate by Cornelisse *et al.* [10] for nucleophilic aromatic photo-substitutions. The present evidence does not allow us to choose between these alternatives.

Soumillion and De Wolf [5] have suggested a common mechanism for photosubstitution and photoreduction involving the formation of a pair of radical ions via a triplet excimer. This proposal is in disagreement with the present results, since their mechanism implies a dependence of the quantum yield on the chlorobenzene concentration. Moreover, oxygen quenches the photoreduction but not the photosubstitution reaction.

In agreement with our findings, Kulis *et al.* [3] report that in the photolysis of chlorobenzene in EtOH-H₂O (1:7) phenol is formed with a quantum yield of 0.08 and that there is no effect of pH and dissolved oxygen. However, they failed to notice the quenching effect of oxygen on the photoreduction in methanol and ascribed both processes as being originated

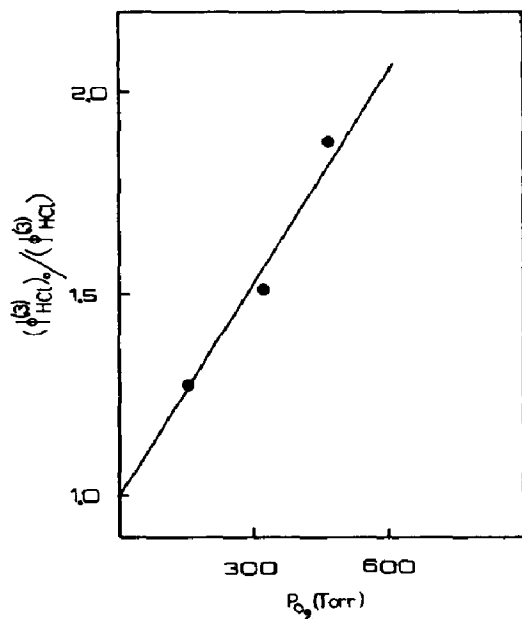


Fig. 2. Effect of oxygen on the quantum yields for the production of HCl from the triplet state for the photolysis of chlorobenzene at 254 nm in 25%EtOH-H₂O.

in the excited singlet state. The direction of the photoreaction was supposed to be determined by the nature of the solvate of the chlorobenzene in its ground state [3].

In Fig. 2 a typical Stern-Volmer plot

$$\frac{(\phi_{\text{HCl}}^{(3)})_0}{\phi_{\text{HCl}}^{(3)}} = 1 + k_q \tau_0 [\text{O}_2] \quad (2)$$

is shown for the quantum yield $\phi_{\text{HCl}}^{(3)}$ of HCl arising from the triplet state versus the oxygen pressure. $\phi_{\text{HCl}}^{(3)}$ was calculated from

$$\phi_{\text{HCl}}^{(3)} = \phi_{\text{HCl}} - (\phi_{\text{phenol}} + \phi_{\text{phenetole}}) \quad (3)$$

From the slopes of the plots for the various solvent mixtures the triplet lifetimes τ_0 were estimated with a value of $3.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ assumed for the bimolecular rate constant of the quenching process [11]. The results

TABLE 2

Quantum yields for the production of HCl from the triplet state and triplet lifetimes for chlorobenzene in EtOH-H₂O mixtures

Solvent	$\phi_{\text{HCl}}^{(3)}$	$\tau (\times 10^{-8} \text{ s})$
H ₂ O	0.04	9.0
H ₂ O-25%EtOH	0.07	3.0
H ₂ O-50%EtOH	0.16	1.9
H ₂ O-75%EtOH	0.23	1.6

are shown in Table 2 together with $(\phi_{\text{HCl}}^{(3)})_0$. The values of τ_0 in EtOH-H₂O are one order of magnitude lower than those reported in cyclohexane [6].

The intersystem crossing quantum yield in cyclohexane was estimated [6] to be 0.64. From studies on other aromatic compounds it can be assumed that the triplet yield is fairly independent of the solvent polarity [12]. If it is supposed on these grounds that, in our solvent mixtures the intersystem crossing quantum yield is nearly constant and around 0.6, then the increase in the quantum yields on going to the less polar solvent may reflect an enhancement in the extent of the homolytic bond cleavage compared with other decay routes for the triplet state. This is in accordance with the shorter lifetimes of the triplet state shown in Table 2.[†]

A point in apparent contradiction with the proposed reaction scheme is the sensitization effect of aliphatic ketones on the photolysis of chlorobenzene in EtOH [5] and cyclohexane [13]. It has also been observed that chlorobenzene in water, irradiated at 313 nm in the presence of acetone, affords HCl and phenol [14]. If this sensitization involved energy transfer from the ketone triplet to chlorobenzene then the mechanism proposed in this work could not be supported. However, it has been shown that the quenching of ketone triplets by chlorobenzene does not follow the pattern of a normal endothermic energy transfer [15]. This sensitization deserves further investigation, although it seems that it cannot be regarded as a simple homolysis of the triplet state of chlorobenzene.

In conclusion, we propose that, when chlorobenzene is irradiated at 254 nm in EtOH-H₂O mixtures, it undergoes a photosubstitution reaction from the singlet state, which involves electrophilic attack to the solvent by a very reactive intermediate. Simultaneously a homolytic bond rupture in the triplet state takes place, the extent of which increases with decreasing solvent polarity.

Acknowledgments

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[†] An alternative explanation suggested by one of the referees is to assume that, once ³ClPh* has been formed, its decomposition efficiency is solvent independent. The quantum yield of the photoreduction will then vary with solvent, increasing as the concentration of EtOH increases, because the intersystem crossing quantum yield would increase with increasing EtOH concentration.

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