

PHOTOLYSIS OF DICHLOROBENZENE VAPOUR IN THE PRESENCE OF ETHANE

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Summary

The photodecomposition of gas-phase *o*-, *m*- and *p*-dichlorobenzene in the presence of ethane at 253.7 nm was investigated. The quantum yields of the dissociation of the C—Cl bond on irradiation at 253.7 nm were estimated to be 0.90, 0.82 and 0.90 for *p*-dichlorobenzene, *m*-dichlorobenzene and *o*-dichlorobenzene respectively, for ethane pressures higher than 200 Torr. The photodissociation quantum yield of *p*-dichlorobenzene shows a dependence on the pressure of ethane (up to 200 Torr) that is different from that of the other isomers, and this is attributed to collision-induced decomposition.

1. Introduction

By studying the photolysis of monochlorobenzene vapour at 253.7 nm it has been shown that excited molecules predominantly undergo non-radiative transitions that lead to the dissociation of the C—Cl bond with a quantum yield of 0.4 [1]. The fluorescence quantum yield, which is less than 10^{-2} , and the short fluorescence lifetime are almost insensitive to the pressure of a foreign gas (ethane) for excitation at 253.7 nm [2]. The non-radiative transition seems to consist exclusively of intersystem crossing to triplet levels of high vibrational energy. It is thought that the triplet molecules thus formed undergo unimolecular decomposition or are raised to vibrationally excited levels of the ground electronic state. The unimolecular decomposition and the non-radiative transition in monochlorobenzene molecules excited at 253.7 nm are almost independent of the pressure of ethane [1]. Most of these fast intramolecular transitions seem to be induced by the chlorine atom substituent of the benzene ring.

A recent study on the photolysis of chlorotoluene (which has the methyl substituent on the monochlorobenzene ring) indicated that the photodecomposition quantum yields are close to unity under collision-free conditions and decrease with increasing pressure of ethane when the mole-

cules of *p*-, *m*- and *o*-chlorotoluene are excited at 253.7 nm [3]. The sensitized phosphorescence of biacetyl by triplet chlorotoluene molecules in the vapour phase has been observed previously [4, 5]. The quantum yield of thermalized triplet formation increased with increasing pressure of ethane [5]. Thus it is believed that the triplet chlorotoluene molecules initially formed by intersystem crossing from the optically excited singlet state undergo photodecomposition or collisional relaxation to the stable triplet levels. Of the three isomers of chlorotoluene the *p*-isomer has the smallest photodecomposition rate constant [3, 5]. The methyl substituent is the cause of lifetimes for vibrationally excited triplet chlorotoluene molecules being longer than for monochlorobenzene; this effect is attributed to the increased degree of internal freedom of motion.

It was expected that the introduction of an additional chlorine atom into the monochlorobenzene ring would increase the number of non-radiative transitions. However, measurements of the fluorescence quantum yields (about 10^{-2}) and lifetimes (about 1 ns) of the excited singlet states of dichlorobenzenes indicate that increasing the number of chlorine atoms does not strongly enhance intersystem crossing but that the fluorescence quantum yield and the lifetime are dependent upon the position of the second chlorine atom substituent (the influence of the symmetry of the molecule [6]). The quantum yields of fluorescence and the excited-singlet lifetimes are quite similar for chlorotoluenes [7] and dichlorobenzenes. As with other disubstituted benzenes [8], *p*-chlorotoluene in its first excited singlet state has a fast radiative transition rate compared with those of *o*- or *m*-chlorotoluenes.

Preliminary results on the excitation of *p*-dichlorobenzene at 253.7 nm indicated a collision-induced decomposition for the excited molecules [9]. In this paper we describe the results in more detail together with the studies of the photolysis of other dichlorobenzenes.

2. Experimental details

The experimental system has been described in a previous paper [9]. The number of light quanta absorbed by the sample is determined from the absorption intensity of the sample and the intensity of the light incident on the reaction cell. The absorption coefficients of the samples at 253.7 nm were determined as $6.5 \times 10^{-3} \text{ Torr}^{-1} \text{ cm}^{-1}$, $6.0 \times 10^{-3} \text{ Torr}^{-1} \text{ cm}^{-1}$ and $7.1 \times 10^{-3} \text{ Torr}^{-1} \text{ cm}^{-1}$ for *p*-dichlorobenzene, *m*-dichlorobenzene and *o*-dichlorobenzene respectively. The absorption coefficient of *p*-dichlorobenzene vapour at 184.9 nm was about $1.3 \text{ Torr}^{-1} \text{ cm}^{-1}$. The incident light intensity was measured by means of a chemical actinometer using potassium ferrioxalate (at 253.7 nm) or N_2O (at 184.9 nm).

The pressure of the sample was kept at its vapour pressure at 0 °C (*p*-dichlorobenzene, 0.13 Torr; *m*-dichlorobenzene, 0.29 Torr; *o*-dichlorobenzene, 0.27 Torr). The temperature of the reaction system was maintained at 70 °C to avoid adsorption of sample molecules on the cell wall. Ethane

was added to the sample vapour to scavenge free radicals and atoms produced by the photolysis [1] and also to investigate the effects of intermolecular collisions. In order to prevent secondary reactions of the products the irradiation time was limited so that the conversion of the sample did not exceed 20%. The products (except hydrogen chloride) were analysed using gas chromatography. In some experiments, CO_2 or SF_6 was added to the mixture of the *p*-dichlorobenzene vapour and ethane to provide a chemically inactive collision partner.

3. Results and discussion

3.1. Photodecomposition quantum yields of dichlorobenzenes

In the presence of ethane, the photolyses of *p*-, *m*- and *o*-dichlorobenzene at 253.7 nm gave detectable amounts of the products monochlorobenzene, ethylene and *n*-butane. In the absence of ethane, the photolyses of the dichlorobenzenes produced polymeric substances on the cell wall, probably through complicated secondary reactions of the initial photoproducts, and hence the products were not analysed. In the presence of ethane, the amounts of photoproducts increased linearly with increasing irradiation time within the conversion limit.

In Fig. 1(a) the quantum yields $\Phi(\text{C}_6\text{H}_5\text{Cl})$, $\Phi(\text{C}_4\text{H}_{10})$ and $\Phi(\text{C}_2\text{H}_4)$ of monochlorobenzene, *n*-butane and ethylene respectively are plotted against the pressure of ethane. For *m*- and *o*-dichlorobenzene, values were also plotted for the pressure of ethane in Figs. 1(b) and 1(c): the plots for $\Phi(\text{C}_4\text{H}_{10})$ and $\Phi(\text{C}_2\text{H}_4)$ were omitted but the results for *m*- and *o*-dichlorobenzene were very similar to those for *p*-dichlorobenzene. The results in Fig. 1 led to the relations

$$\Phi(\text{C}_6\text{H}_5\text{Cl}) \approx \Phi(\text{C}_4\text{H}_{10}) + \Phi(\text{C}_2\text{H}_4) \quad (1)$$

$$\Phi(\text{C}_2\text{H}_4)/\Phi(\text{C}_4\text{H}_{10}) \approx 0.17 \quad (2)$$

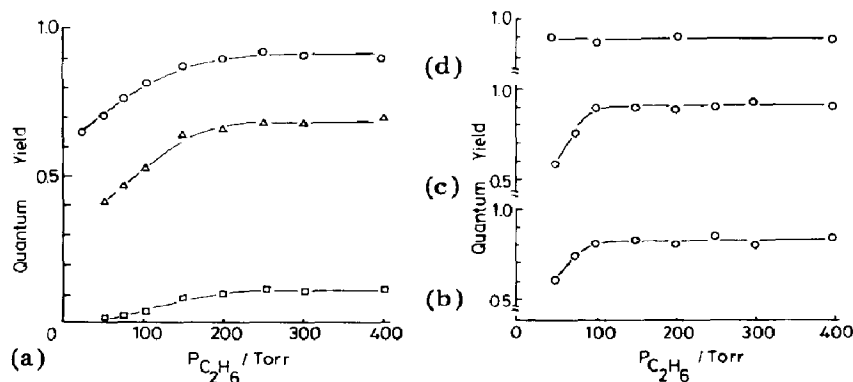


Fig. 1. Effect of ethane pressure on the quantum yields of the photoproducts in the photolyses at 253.7 nm of (a) *p*-dichlorobenzene, (b) *m*-dichlorobenzene, (c) *o*-dichlorobenzene and (d) in the photolysis of *p*-dichlorobenzene at 184.9 nm: \circ , $\Phi(\text{C}_6\text{H}_5\text{Cl})$; \triangle , $\Phi(\text{C}_4\text{H}_{10})$; \square , $\Phi(\text{C}_2\text{H}_4)$.

These results indicate that the photochemical reaction of dichlorobenzene molecules excited at 253.7 nm is initiated by the dissociation of the C—Cl bond to form chlorophenyl radicals and chlorine atoms as has been reported for monochlorobenzene and chlorotoluenes [1, 3]. Chlorophenyl radicals and chlorine atoms form monochlorobenzene and hydrogen chloride by hydrogen-atom abstraction reactions with ethane. Ethyl radicals formed in this process undergo recombination reactions to form butane or disproportionation reactions to form ethylene and ethane, similarly to the photolysis of monochlorobenzene [1] since $\Phi(\text{C}_2\text{H}_4)/\Phi(\text{C}_4\text{H}_{10}) \approx 0.17$. The ratio of disproportionation to recombination reactions for ethyl radicals is in good agreement with literature values [10].

The relation given in eqn. (1) confirms that the C—Cl bond dissociation quantum yield is given by the constant value $\Phi(\text{C}_6\text{H}_5\text{Cl})$ of the formation yield for monochlorobenzene at high ethane pressures. The values at 253.7 nm are 0.90 for *p*-dichlorobenzene, 0.82 for *m*-dichlorobenzene and 0.90 for *o*-dichlorobenzene. These values indicate that dichlorobenzene molecules excited at 253.7 nm predominantly undergo dissociation into chlorophenyl radicals and chlorine atoms, probably via triplet states even in the presence of ethane [11].

At low ethane pressures, $\Phi(\text{C}_6\text{H}_5\text{Cl})$ is low but it increases with the ethane pressure indicating incomplete conversion of chlorophenyl radicals to monochlorobenzene. The conversion of chlorophenyl radicals to monochlorobenzene seems to be complete for the photolyses of *m*- and *o*-dichlorobenzene in the presence of more than 100 Torr ethane (Figs. 1(b) and 1(c)). In the photolysis of *p*-dichlorobenzene at 184.9 nm, $\Phi(\text{C}_6\text{H}_5\text{Cl})$ reaches a constant value at about 50 Torr ethane (Fig. 1(d)). In the photolysis of monochlorobenzene at 253.7 nm and 184.9 nm, the pressure dependences of $\Phi(\text{C}_6\text{H}_6)$ are very similar and constant for a pressure of more than 50 Torr ethane [1]. Therefore, the conversion of *p*-chlorophenyl radicals to monochlorobenzene is expected to be complete at ethane pressures higher than 100 Torr.

The value of $\Phi(\text{C}_6\text{H}_5\text{Cl})$ for the photolysis of *p*-dichlorobenzene, however, increases gradually with ethane pressure up to about 200 Torr and reaches a constant value of about 0.9 (Fig. 1(a)). This discrepancy cannot be explained by the chemical reactivity of the chlorophenyl radicals since the steric effect due to the bulky chlorine atom in the free radical would seem to indicate a higher chemical reactivity for *p*-chlorophenyl radicals than for those of the other isomers. Another explanation for this result is the collision-induced decomposition of excited *p*-dichlorobenzene molecules at 253.7 nm. The higher molecular symmetry may inhibit the decomposition of excited *p*-dichlorobenzene molecules. The intermolecular collisions induce cross energy transfer to vibronic levels of different symmetry species, and decomposition can then take place.

3.2. Collision-induced decomposition of *p*-dichlorobenzene

In order to examine the collision-induced decomposition, chemically inactive molecules such as CO_2 and SF_6 were added to the mixture of *p*-

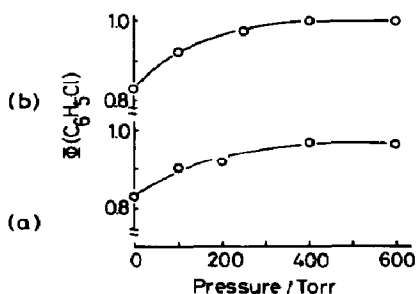
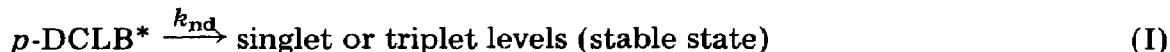


Fig. 2. Pressure effects of (a) SF₆ and (b) CO₂ on $\Phi(C_6H_5Cl)$ in the photolysis of the mixture of *p*-dichlorobenzene and ethane (100 Torr) at 253.7 nm.

dichlorobenzene and ethane (pressure, 100 Torr). The addition of 400 Torr CO₂ resulted in an increase in $\Phi(C_6H_5Cl)$ from 0.83 to 1.0 as shown in Fig. 2. Analogous results induced by the addition of SF₆ are also shown in Fig. 2. Similar experiments in the presence of 50 Torr ethane also showed the increase in $\Phi(C_6H_5Cl)$ with pressure of CO₂ or SF₆. However, photolyses of *o*- and *m*-dichlorobenzene with ethane (pressure, 50 Torr and 100 Torr respectively) did not exhibit such an increase in the value of $\Phi(C_6H_5Cl)$, even for the addition of CO₂ or SF₆ to 760 Torr. These results clearly indicate that molecular collisions between excited *p*-dichlorobenzene molecules and CO₂ or SF₆ induce the decomposition of excited *p*-dichlorobenzene into free radicals and atoms.

A phenomenological reaction mechanism for excited *p*-dichlorobenzene (*p*-DCLB*) molecules can be expressed as



where M denotes a collision partner. Reaction process (I) includes all non-decomposition processes and reaction (II) includes collision-induced decompositions and collisional relaxation to non-decomposing states. Since the value of $\Phi(C_6H_5Cl)$ at ethane pressures higher than 100 Torr is presumably related to the quantum yield of *p*-chlorophenyl radical formation, the increased amount of $\Phi(C_6H_5Cl)$ in Fig. 2 can be attributed to reaction (II). The contribution of the collision-induced decomposition rate to the value of k_d cannot be obtained quantitatively from the present experimental results, but it must be large.

The increased value of $\Phi(C_6H_5Cl)$ for CO₂ in Fig. 2 seems to be the largest among the three collision partners. This suggests that CO₂ is a more efficient partner in collision-induced decompositions than ethane or SF₆. However, the collisional-quenching rate constant of CO₂ is generally believed to be the smallest among the three molecules. This discrepancy seems to indicate that collision-induced decomposition may proceed only through weak collisions which cause a breakdown of the high molecular symmetry in *p*-dichlorobenzene. The different symmetry of the vibronic levels of the

excited molecules may cause the difference in coupling between the excited levels and the dissociation continuum.

3.3. Photoisomerization of *p*-dichlorobenzene to *m*-dichlorobenzene

When the irradiation time for the light of wavelength 184.9 nm was prolonged for an extremely long time in a photolysis of the *p*-dichlorobenzene-ethane mixture, a very small amount of *m*-dichlorobenzene was detected. Our observation that the amount of *m*-dichlorobenzene increased linearly with the irradiation time indicates that this process is not due to secondary reactions. Although the quantum yield of isomerization could not be determined accurately, it is estimated to be of the order of 10^{-4} . This is also consistent with the fact that the quantum yield of photodecomposition is nearly unity and its sensitivity to low pressures indicates that the excited *p*-dichlorobenzene has a short lifetime.

It is possible to form the *m*-isomer by a mechanism involving free radicals such as *p*-chlorophenyl. However, this would not be a feasible process with excess ethane; it is more likely that some intramolecular processes are involved. Wilzbach and Kaplan [12] reported that photoisomerization of xylenes in the vapour phase takes place intramolecularly, probably through a benzvalene intermediate. Horrocks *et al.* [13] found from isotopic labelling experiments that the rearrangement is intramolecular and that the movement of the ring carbon atoms takes place at the same time as the migration of the methyl groups. It is not possible to determine the isomerization intermediate for the photolysis of *p*-dichlorobenzene. There are six possible pathways in which benzvalene may be formed from a benzene structure. 1,3-Dichlorobenzvalene and 2,5-dichlorobenzvalene can be formed starting from *p*-dichlorobenzene, and relaxation of these benzvalene intermediates may give rise to the formation of *m*- and *p*-dichlorobenzene.

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