PHOTOLYSIS OF CHLOROTOLUENE VAPOUR IN THE PRESENCE OF ETHANE

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Summary

The photodecomposition of *o-*, *m-* and *p*-chlorotoluene was investigated at 253.7 nm in the presence of ethane. The quantum yields of the C—Cl bond dissociation of these molecules were found to be close to unity under collision-free conditions and to decrease with increases in the ethane pressure. The rate constant of photodecomposition was estimated from the Stern–Volmer plots of the formation quantum yield of the photoproduct (toluene). The smallest value of the rate constant was obtained for *p*-chlorotoluene. The methyl substituent on the monochlorobenzene ring causes long lifetimes for the excited molecules which undergo decomposition.

1. Introduction

A study of the photolysis of monochlorobenzene vapour has revealed that molecules excited at 253.7 nm predominantly undergo decomposition into phenyl radicals and chlorine atoms with a quantum yield of 0.4 [1]. A small fluorescence quantum yield less than 10^{-2} and a short fluorescence lifetime were almost insensitive to the pressure of ethane when molecules were excited at 253.7 nm [2]. Most optically excited monochlorobenzene molecules are thus supposed to be converted into the triplet state with high vibrational energy [2]. The triplet molecules then seem to undergo unimolecular decomposition to form radicals and atoms or undergo nonradiative transitions leading the molecules into vibrationally excited levels of the ground electronic state. The unimolecular decomposition and the nonradiative transitions in monochlorobenzene molecules excited at 253.7 nm are believed to be very fast because, at higher pressures of ethane, the photoproduct quantum yields are independent of further increases in the ethane pressure [1]. These fast intramolecular transitions are induced by the chlorine atom substituent on the benzene ring.

The introduction of the additional chlorine atom into the monochlorobenzene ring was expected to enhance the non-radiative transitions further.

The fluorescence measurements of dichlorobenzenes in the vapour phase, however, suggested a small enhancement in the non-radiative transitions in optically excited dichlorobenzene molecules compared with those in monochlorobenzene molecules [3]. The fluorescence quantum yield and the lifetime of the excited singlet molecules are sensitive to the position of the second chlorine atom substituent, an effect attributed to molecular symmetry.

The quantum yields of fluorescence and the lifetimes of the optically excited chlorotoluenes are quite similar to those of the dichlorobenzenes [4]. p-Chlorotoluene in its first excited singlet state has a fast radiative rate compared with that of o- or m-chlorotoluenes similarly to other disubstituted benzenes [5 - 9]. The rates of intersystem crossing from the excited singlet states to the triplet states in chlorotoluene molecules seem to be determined predominantly by the chlorine atom substituent and only slightly by the methyl substituent [4]. However, the decomposition rate of triplet chlorotoluene molecules does not necessarily require intersystem crossing to the singlet ground state and may be affected by the methyl substituent. The increased degree of internal freedom of motion and the modification of molecular symmetry by the methyl substituent are supposed to have important effects on the decomposition of triplet chlorotoluene molecules. The purpose of the present study is to examine the effect of the methyl substituent on the primary photochemical processes in the photodecomposition of chlorine-substituted benzenes.

2. Experiment

The experimental system is the same as that reported in a previous paper [10]. The values of the absorption coefficients at 253.7 nm were determined to be 4.2×10^{-3} Torr^{-1} cm^{-1}, 1.7×10^{-3} Torr^{-1} cm^{-1} and 4.6×10^{-3} Torr^{-1} cm^{-1} for o-chlorotoluene, m-chlorotoluene and p-chlorotoluene respectively. The potassium ferrioxalate chemical actinometer was used to determine the light intensity at 253.7 nm. The pressure of each sample was kept at the vapour pressure at 0 °C (0.6 Torr for the three isomers) and 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 chlorotoluene vapour to scavenge the free radicals or atoms produced by photodecomposition [1] and also to investigate the effect of collisional relaxation. CO_2 was added in some experiments to the mixture of chlorotoluene vapour and ethane as a chemically inactive collision partner.

3. Results and discussion

In the presence of ethane, photodecomposition of o-, m- and p-chlorotoluenes at 253.7 nm gave detectable products such as toluene, butane and

ethylene. A probable product, hydrogen chloride, was not analysed. In the absence of ethane the photodecomposition of chlorotoluenes seemed to be much more complicated, which is evident by the formation of polymers on the cell wall. To prevent complex secondary reactions the irradiation time was limited so that the amount of toluene formed by the photodecomposition did not exceed 20% of the initial amount of the sample. Within this conversion limit the amounts of photoproducts increased linearly with the irradiation time. It is clearly understood that the photochemical reaction of chlorotoluenes excited at 253.7 nm is initiated by the C—Cl bond dissociation to yield $C_6H_4CH_3$ radicals and chlorine atoms as are those of monochlorobenzene and dichlorobenzenes [1, 10]. $C_6H_4CH_3$ radicals and chlorine atoms can form $C_6H_5CH_3$ and hydrogen chloride by hydrogen abstraction reactions with ethane. Therefore, if enough ethane exists, the quantum yield of toluene is expected to be equal to the C—Cl bond dissociation quantum yield of optically excited molecules. This was also confirmed by the fact that the value of the toluene quantum yield is close to the sum of the quantum yields for formation of ethylene and butane in the presence of ethane at 100 - 400 Torr [1].

The quantum yields of toluene formed in the chlorotoluene photolyses at 253.7 nm are plotted against the pressure of ethane in Fig. 1. The quantum yields increase with increases in the pressure of ethane up to 100 Torr and then gradually decrease for further increases in the ethane pressure. This increase in the quantum yield at low ethane pressures shown in Fig. 1 can be simply interpreted by incomplete conversion of atoms and free radicals to stable molecular products (chlorine atoms to hydrogen chloride and $C_6H_4CH_3$ to $C_6H_5CH_3$) by hydrogen abstraction reaction with ethane. In the presence of ethane at around 100 Torr, the conversion of unstable fragments seems to be complete.

The gradual decrease in the quantum yield of toluene at higher ethane pressures is attributed to the collisional deactivation of excited chlorotoluene molecules. The quantum yield of toluene formation also decreases with further additions of CO_2 as a second foreign gas to the mixture of
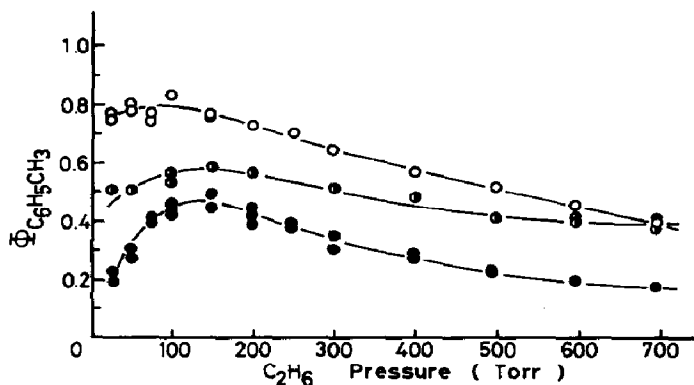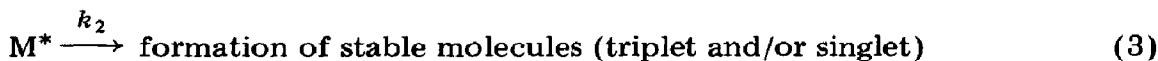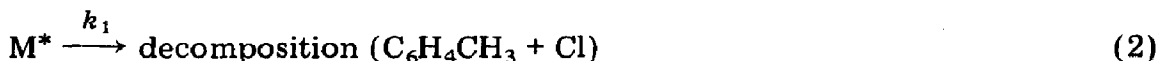
Fig. 1. The pressure effect of the photoproduct (toluene) quantum yields by ethane: ●, p-chlorotoluene; ○, m-chlorotoluene; ◑, o-chlorotoluene.

chlorotoluene vapour and ethane (the ethane pressure was 100 Torr for *o*- or *p*-chlorotoluene and 50 Torr for *m*-chlorotoluene). For both foreign gases (ethane and CO_2) the decreasing trends in the toluene quantum yield are most pronounced in the *p*-chlorotoluene photodecomposition. A similar foreign gas effect on the photodecomposition was observed very slightly in the photolysis of benzyl chloride vapour but was scarcely observable in the photolyses of monochlorobenzene [1] and *o*- or *m*-dichlorobenzene [10]. The opposite collisional effect was observed in the photolysis of *p*-dichlorobenzene [10].

At higher ethane pressures, the formation quantum yield of toluene would be regarded as the decomposition quantum yield of excited chlorotoluene molecules. The reciprocal of the quantum yield of toluene formation (the photodecomposition quantum yield Φ_D) was plotted against the pressure of ethane for pressures above 100 Torr. The plots give straight lines as shown in Fig. 2. These results indicate that collisional relaxation of excited chlorotoluene molecules by ethane competes with the decomposition of excited chlorotoluene molecules.

Thus a phenomenological simple reaction mechanism can be written as follows (M* is an excited molecule and X is a foreign gas molecule):

$$M + h\nu \longrightarrow M^* \tag{1}$$

$$M^* \xrightarrow{k_1} \text{decomposition } (C_6H_4CH_3 + Cl) \tag{2}$$

$$M^* \xrightarrow{k_2} \text{formation of stable molecules (triplet and/or singlet)} \tag{3}$$

$$M^* + X \xrightarrow{k_3} \text{formation of stable molecules (triplet and/or singlet)} \tag{4}$$

Reaction (4) might involve vibrational relaxation within the same electronic state but in this simple reaction scheme it does not have any significant
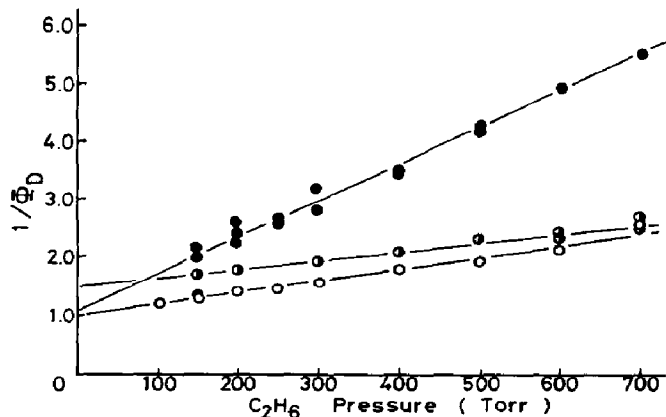

Fig. 2. Stern–Volmer plots for photodecomposition quenching by ethane (Φ_D is the quantum yield of photodecomposition and is equal to the yield of toluene): ●, *p*-chlorotoluene; ○, *m*-chlorotoluene; ◑, *o*-chlorotoluene.

effect on the explanation of the experimental results. Reactions (1) - (4) can lead to the relation

$$\frac{1}{\Phi_D} = \frac{k_1 + k_2}{k_1} + \frac{k_3}{k_1}[X]$$

This relation can explain the experimental results in Fig. 2. Values of k_3/k_1 and $(k_1 + k_2)/k_1$ are obtained from the slope and the intercept respectively. If the rate constant k_3 for deactivation of excited chlorotoluene molecules by ethane is approximated by the hard sphere collision frequency with a collisional cross section of 25 Å^2, values of k_1 and k_2 can be calculated as listed in Table 1. The values of k_1 in Table 1 should be regarded as the largest limiting values, however, since a unit efficiency for the deactivation collisions of the excited chlorotoluene molecules has been assumed in the calculation of k_3.

TABLE 1

Summary of the photodecomposition rate constants for chlorotoluenes and benzyl chloride

	o-chlorotoluene[a]	m-chlorotoluene[a]	p-chlorotoluene[a]	Benzyl chloride[b]
k_2/k_1	0.5	0	0.1	0.1
$\Phi_D(P_{C_2H_6} = 0)$	0.7	1.0	0.9	0.9
k_3/k_1[c] (M^{-1})	34	45	136	17
k_1 ($\times 10^9 \text{ s}^{-1}$)	7.1	5.3	1.8	11

[a] This work.
[b] Previous work [11].
[c] k_3 was estimated from the hard sphere collision frequency ($k_3 = 4.73 \times 10^{10}\sigma^2/\mu^{1/2}$ $\text{M}^{-1}\text{ s}^{-1}$): $k_3 = 2.4 \times 10^{11}$ $\text{M}^{-1}\text{ s}^{-1}$ and $k_3 = 1.9 \times 10^{11}$ $\text{M}^{-1}\text{ s}^{-1}$ for chlorotoluene–ethane and benzyl chloride–butane systems respectively, where $\sigma^2(\text{CH}_3\text{C}_6\text{H}_4\text{Cl}-\text{C}_2\text{H}_6) = \sigma^2(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}-\text{C}_4\text{H}_{10}) = 25$ Å^2 and μ is the reduced mass.

In Table 1 the values of k_1 indicate short lifetimes for chlorotoluene molecules excited at 253.7 nm, which are presumably in excited singlet states. The fluorescence lifetimes of chlorotoluene vapours excited at 253.7 nm are very short and are supposed to be less than 1 ns from observed values at longer excitation wavelengths [4]. The lifetimes of the excited states of chlorotoluenes, however, seem to be much longer (by a factor of 10 - 100) than those given by the values in Table 1 since the efficiency of the deactivating collisions is less than unity as shown below.

In the vapour phase photolysis of benzyl chloride at 253.7 nm Stern–Volmer plots of the product yield against the pressure of the added butane have led to a lifetime for the decomposing state of about 0.1 ns [11]. The lifetime of the benzyl chloride fluorescence excited at 253.7 nm is short and estimated to be less than 1 ns from the fluorescence decay curve. (In a previous study [12] the decay curves and quantum yields for the fluorescence of benzyl chloride were measured. The fluorescence decay was

represented by two components; the lifetimes were 1.3 and 20 ns at 268 nm excitation.) However, the rise time of the fragment (benzyl radical) absorption observed at 305 nm is about 6 ns under collision-free conditions and the collisional deactivating rate constant of excited benzyl chloride molecules is estimated to be of the order of $10^9 - 10^{10} \, M^{-1} \, s^{-1}$ in the vapour phase laser photolysis [13]. This value is one or two orders of magnitude smaller than that of the hard sphere collision frequency. This suggests that chlorotoluene molecules excited at 253.7 nm decompose with longer lifetimes of about 10 ns or more.

The fluorescence lifetimes of the chlorotoluene isomers estimated from fluorescence quantum yields by the 253.7 nm excitation fall into a rather narrow range from 0.3 to 0.6 ns [4] and do not correspond to the relative lifetimes deduced from the values of k_1 and k_2 listed in Table 1. The collisional deactivation of chlorotoluene molecules excited at 253.7 nm therefore seems to be significant in the triplet states which are formed by the intersystem crossing from the initially excited singlet state.

The short lifetimes of the excited singlet chlorotoluene molecules of 0.3 - 0.6 ns are determined by the rates of intersystem crossing to triplet states and/or by that of internal conversion to the ground state. High quantum yields of stabilized triplet molecules have been obtained from the observation of photosensitized phosphorescence of biacetyl vapour by chlorotoluene in the presence of high pressures of foreign gases [14]. The relative stabilization rate constants for the initially formed triplet molecules with excess vibrational energy from collisions approximately corresponded to the values of k_1 listed in Table 1. In view of the fact that the fast non-radiative process in the excited singlet chlorotoluenes has been induced by the chlorine atom substituent, most of the optically excited chlorotoluene molecules are converted to triplet states and then undergo various photophysical and photochemical processes.

The 253.7 nm photodecomposition of chlorotoluene vapours is quenched by ethane at high pressures although those of monochlorobenzene [1] and o- and m-dichlorobenzene did not exhibit quenching sensitivity towards ethane [10]. The high pressure sensitivity of chlorotoluene molecules can be attributed to the long lifetimes of the excited triplet molecules. This is probably due to additional low frequency vibrational modes introduced by methyl substitution and effective intramolecular vibrational relaxation.

In dichlorobenzenes and also in chlorotoluenes, *para* isomers have the highest sensitivity to the pressure effect on the vapour phase photolysis at 253.7 nm. This seems to indicate that *para* isomers have longer lifetimes than *ortho* or *meta* isomers in their excited triplet states. The difference in sensitivity between the photolysis of p-dichlorobenzene, where the photodecomposition is induced by collision, and the photolysis of p-chlorotoluene, in which the photodecomposition is quenched by collision, may be due to the difference in the effective number of low frequency vibrational modes.

The unexpectedly small photodecomposition quantum yield of *o*-chlorotoluene vapour under collision-free conditions is interpreted in part by the formation of benzyl radicals through isomerization of *o*-tolyl radicals. This isomerization process was investigated by Brenner *et al.* [15] who observed the laser-induced fluorescence of benzyl radicals for the reaction of barium atoms and *o*-chlorotoluene. They suggested that about 30% of the *o*-tolyl radicals were converted to benzyl radicals by intramolecular migration of the hydrogen atoms. In the photodecomposition of *o*-chlorotoluene, the fragment *o*-tolyl radicals can isomerize to benzyl radicals before the excess vibrational energy is thermalized. If 30% of the *o*-tolyl radicals are lost by the isomerization and the benzyl radicals produced cannot abstract hydrogen atoms from ethane, the initial quantum yield of the photodecomposition under collision-free conditions is expected to be close to unity.

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