FORMATION OF METHYLANISOLE IN THE PHOTOLYSIS OF CHLOROTOLUENE IN METHANOL

TEIJIRO ICHIMURA, MASAYOSHI IWAI and YUJI MORI

Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152 (Japan)

Summary

Photolyses of *p*-, *m*- and *o*-chlorotoluene in methanol gave formation quantum yields of methylanisoles of the order of 10^{-2}, which are substantially smaller than that for chlorobenzene. The values for the para and ortho isomers are smaller than that for the meta isomer. This result can be explained in terms of the effect of the methyl substituent, which induces negative charges at the ortho and para positions. The effect of biacetyl addition was also examined and the results indicated that the triplet route is significant, as in the case of chlorobenzene. However, about half the methylanisole was formed without any dependence on the biacetyl concentration, indicating the presence of an intermediate state with a very short lifetime.

1. Introduction

The photochemistry of chloroaromatics has been extensively studied because of its importance in environmental pollution [1]. The excited state of chlorobenzene dominantly photodissociates via its triplet states to a phenyl radical and a chlorine atom [2]. The photodecomposition quantum yield has been reported to be 0.4 in the gas phase photolysis at 253.7 nm [2] and 0.3 - 0.4 in cyclohexane solutions [3 - 6]. In hydroxylic solvents, however, photoreduction and photosubstitution by the solvent occur simultaneously [7 - 9]. Recently, Nagaoka *et al.* [10] reported that the photosubstitution of chlorobenzene by methanol takes place in the triplet (π, σ^*) molecules, but Previtali and Ebbeson [11] suggested that an intermediate, the radical cation of chlorobenzene formed via singlet excited states, seems to be important in the reaction.

The photosubstitution reaction seems to occur by the nucleophilic attack of methanol on the carbon adjacent to the chlorine atom in the triplet state. Therefore the reaction may be affected by the introduction of an electron donative or attractive substituent on the benzene ring. In this study a methyl substituent was introduced into the chlorobenzene ring and biacetyl

was used as a triplet quencher. Thus we examined the nucleophilic photo-reaction of chlorotoluene with methanol in order to investigate details of this type of reaction.

2. Experimental details

Absorption spectra of p-, m- and o-chlorotoluene in methanol were measured by a JASCO UVIDEC-510 spectrophotometer. The absorption spectra of the subsequent photoproducts, p-, m- and o-methylanisole, were also measured to determine the absorption coefficient. The formation yield of the methylanisole in the photolysis of chlorotoluene in methanol was determined from the measurement of absorption spectra before and after the photolysis. The photolysis was carried out using a monochromatized xenon lamp. The sample solution was introduced into a quartz cell (1 cm square, 4 cm long) and degassed by freeze–pump–thaw cycles in a vacuum line prior to measurements being taken. All the experiments were carried out at room temperature.

Samples of p-, m-, and o-chlorotoluene (stated purity, better than 99%) were obtained from Tokyo Kasei and purified by repeated distillation. Biacetyl was also obtained from Tokyo Kasei and purifed by distillation. Only the middle fraction of the distilled biacetyl was used. The methanol (Spectrograde purity) was obtained from Wako and used without further purification.

3. Results and discussion

Typical examples of the absorption spectra for p-chlorotoluene and p-methylanisole are shown in Fig. 1. The spectrum of the subsequent photo-product, p-methylanisole, is shifted to the red and has a larger absorption coefficient than the parent molecule, p-chlorotoluene. Thus the formation yield can be obtained by the measurement of the absorption spectra before and after irradiation of the sample solution with UV light. A typical differ-ence spectrum (the spectrum before the irradiation subtracted from that after the irradiation) is also shown in Fig. 1 (curve c). The peak of the p-methylanisole absorption is well separated from that of the parent molecule, p-chlorotoluene. Likewise, m-chlorotoluene and o-chlorotoluene in methanol solutions (10^{-3} - 10^{-4} M) were irradiated at 274 nm and 273 nm respectively (±2 nm) and the yields of m-methylanisole and o-methylanisole were mea-sured by their difference absorbances at 279 nm and 277 nm respectively. Here the absorptions of chlorotoluene and methylanisole overlap at these observation wavelengths, so the difference spectrum was simulated by using both absorption spectra and the concentration of methylanisole was esti-mated. The simulation was mainly carried out for wavelengths longer than 260 nm, since some of the other photoproducts absorb at shorter wavelengths.
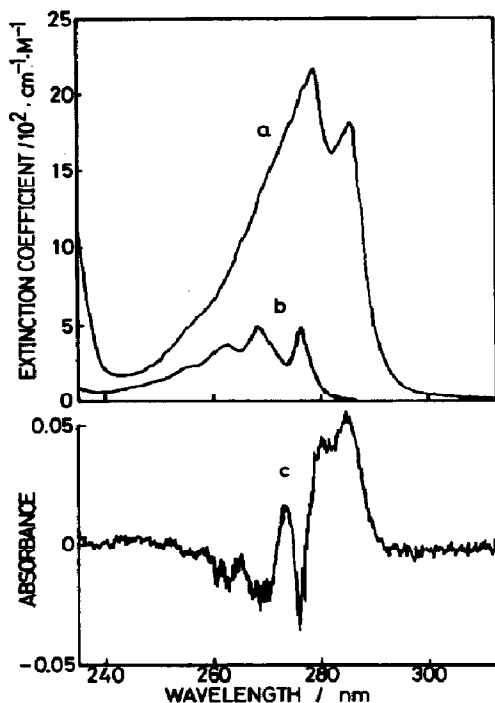
Fig. 1. Absorption spectra of p-methylanisole (curve a) and p-chlorotoluene (curve b) in methanol. Spectrum c is a typical result of the difference absorbance, which was measured by subtracting the spectrum before the photolysis from the spectrum after the 276 nm photolysis of p-chlorotoluene in methanol. The absorption peak at 285 nm in spectrum c corresponds to that of the p-methylanisole formed in the photolysis and the two dips at 276 and 268 nm are due to the depletion of the parent molecule, p-chlorotoluene. The absorption peak of p-methylanisole is well separated from that of p-chlorotoluene, and the formation yield of p-methylanisole can be estimated from the absorbance increase at 285 nm.

TABLE 1

Formation quantum yields Φ of anisole and methylanisoles in photolyses of chlorobenzene and chlorotoluenes in methanol

Molecule	Φ
Chlorobenzene	4.9×10^{-2}
o-Chlorotoluene	2.1×10^{-2}
m-Chlorotoluene	3.2×10^{-2}
p-Chlorotoluene	1.4×10^{-2}

The best-fitting spectrum obtained by the least-squares method represented the observed difference spectrum well. The value of the formation yield (Table 1) has a standard deviation of 20%.

The results of the p-chlorotoluene photolysis show that the yield of p-methylanisole increased in proportion to the irradiation time and to the light quanta absorbed by the sample at a concentration of 10^{-3} - 10^{-4} M.

Similar results were obtained for photolyses of *o*- and *m*-chlorotoluenes. These facts indicate that the photoreaction is induced by the absorption of light by the sample molecules and not by the excitation of the initial products.

The formation quantum yields of *p*-, *m*- and *o*-methylanisole were determined relative to that (0.043) for chlorobenzene [10] and are listed in Table 1. The methylanisole formation quantum yields for chlorotoluenes are smaller than that for chlorobenzene. The values for the para and ortho isomers are smaller than that for the meta isomer. The electron donative effect of the methyl substituent observed in general for the organic chemistry of ground state molecules seems to be similar to that observed in this nucleophilic attack by methanol on the carbon atom adjacent to the chlorine atom. Information concerning the molecular orbital for the excited state of chlorotoluene is required for a more complete discussion.

The quantum yield for the *p*-methylanisole formation was determined to be 0.014, but other reactions, such as photodecomposition, could occur simultaneously. The disappearance yield of *p*-chlorotoluene can be determined from the absorbance dip at 276 nm in the difference spectrum of Fig. 1 since the extinction coefficients are known for both molecules. The value estimated for the disappearance yield is about 0.05. The difference between 0.05 and 0.014 should indicate the occurrence of the photodecomposition.

In order to clarify which reactive excited state forms the methylanisole, various concentrations of biacetyl were added to *p*-chlorotoluene solution in methanol. The quantum yield of *p*-methylanisole formation is plotted against the concentration of biacetyl in Fig. 2. The quantum yield decreased to about half of the initial value on the addition of 10^{-3} M biacetyl but reached a constant value of about 0.007 at concentrations greater than 3×10^{-3} M. Thus the reaction mechanism may be written as follows for the reaction of
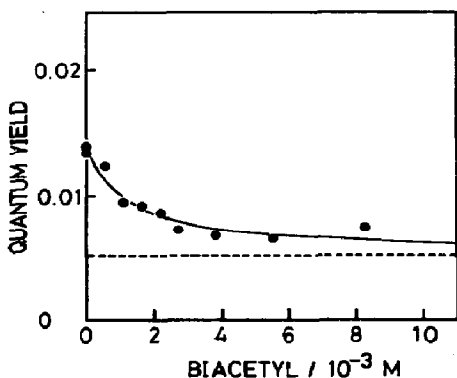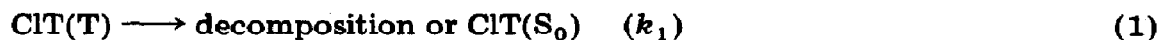

Fig. 2. Plots of formation quantum yields of *p*-methylanisole in the photolysis of *p*-chlorotoluene in methanol (2.8×10^{-3} M) with addition of biacetyl. Full circles show experimental data and the full line indicates the best-fitting curve obtained by the least-squares method using eqn. (I) in the text. The broken line shows the quantum yield for the formation of *p*-methylanisole independent of the biacetyl.

the triplet chlorotoluene (ClT) with biacetyl:

$$ClT(T) \longrightarrow \text{decomposition or } ClT(S_0) \qquad (k_1) \qquad\qquad (1)$$

$$ClT(T) \xrightarrow{\text{CH}_3\text{OH}} MeOT + HCl \qquad (k_2) \qquad\qquad (2)$$

$$ClT(T) + Bi(S_0) \longrightarrow ClT(S_0) + Bi(T) \qquad (k_3) \qquad\qquad (3)$$

where MeOT stands for methylanisole (methoxytoluene) and Bi is biacetyl. On the assumption that the residual methylanisole is formed immediately after the excitation and is not affected by biacetyl, this mechanism leads to the following relation for the formation yield Φ of methylanisole:

$$\Phi = A + \frac{I'k_2}{k_1 + k_2 + k_3[\text{Bi}]}$$

$$\Phi = A + \frac{I'k_2}{(k_1 + k_2)\{1 + k_3[\text{Bi}]/(k_1 + k_2)\}} \qquad\qquad (I)$$

where A denotes the portion of methylanisole formed without any dependence on the biacetyl concentration, I' is the triplet formation rate and [Bi] is the concentration of biacetyl. The results in Fig. 2 can be simulated by using eqn. (I), and this is also shown in the figure (full line). The best-fitting line determined by the least-squares method gives

$$\Phi = 0.0052 + \frac{0.0088}{1 + (7.7 \times 10^2)[\text{Bi}]} \qquad\qquad (II)$$

Thus the ratio of the reaction rate constants can be derived:

$$\frac{k_3}{k_1 + k_2} = 7.7 \times 10^2 \text{ M}^{-1} \qquad\qquad (III)$$

Here the summation of the rate constants $(k_1 + k_2)$ was determined to be about 10^6 s^{-1} from the measurements of the decay of the T–T absorption in methanol solution [12]. (The T–T absorption spectrum of p-chlorotoluene in methanol solution was observed in the wavelength region 250 - 450 nm and the decay of the triplet absorption was measured to be 740 ns.) Accordingly the value of k_3 was evaluated to be about 10^9 M^{-1} s^{-1}. This value is in good agreement with the rate $((1 - 2) \times 10^9$ M^{-1} s$^{-1})$ of quenching of the triplet states of many organic molecules [13] by oxygen. The process of quenching by oxygen is believed to be diffusion controlled. Thus reaction (3) is likely to be diffusion controlled, although diffusional rate constants in methanol are one order of magnitude higher. This discrepancy may arise from the difference between the efficiencies of the quenching processes, since reaction (3) is an electron exchange process. Thus the reaction mechanism discussed above reasonably accounts for part of the methylanisole formed.

Half the methylanisole produced was formed without any dependence on the added biacetyl concentration. This fast formation process has been ob-

served in the photolyses of chlorobenzene [8, 11] and the excited singlet state was postulated as the intermediate state. Two reaction pathways are also likely to occur simultaneously in the photosubstitution of *p*-chlorotoluene. One is the triplet route mentioned above. The other is not clear from the present experimental results. The fluorescence spectra of *p*-chlorotoluene in methanol and cyclohexane were measured under the same conditions and the intensities were carefully compared with each other. No difference, however, could be observed within the experimental error. Thus part of the methylanisole may form from the excited triplet levels. Therefore we may conclude that the fast photosubstitution reaction can take place from the initial excited levels prior to the fast vibrational relaxation in methanol solution.

References

1 A. Gilbert, *Photochemistry*, *8* (1977) 362.
   D. Dulin, H. Drossman and T. Mill, *Environ. Sci. Technol.*, *20* (1986) 72.
2 T. Ichimura and Y. Mori, *J. Chem. Phys.*, *58* (1973) 288.
3 M. A. Fox, W. C. Nichols and D. M. Lemal, *J. Am. Chem. Soc.*, *95* (1973) 8164.
4 D. R. Arnold and D. C. Wong, *J. Am. Chem. Soc.*, *99* (1977) 3361.
5 N. J. Bunce, J. P. Bergsma, M. D. Bergsma, W. DeGraaf, Y. Kumar and L. Ravanal, *J. Org. Chem.*, *45* (1980) 3708.
6 N. J. Bunce, P. J. Hayes and M. E. Lemke, *Can. J. Chem.*, *61* (1983) 1103.
7 J. T. Pinkey and R. D. G. Rigby, *Tetrahedron Lett.*, (1969) 1267.
8 J. Ph. Soumillon and B. Dewolf, *J. Chem. Soc., Chem. Commun.*, (1981) 436.
9 V. Avila, H. E. Gsponer and C. M. Previtali, *J. Photochem.*, *27* (1984) 163.
10 S. Nagaoka, T. Takemura and H. Baba, *Bull. Chem. Soc. Jpn.*, *58* (1985) 2082.
11 C. M. Previtali and T. W. Ebbeson, *J. Photochem.*, *30* (1985) 259.
12 T. Ichimura, M. Iwai and Y. Mori, to be published.
13 I. Carmichael and G. L. Hug, *J. Phys. Chem. Ref. Data*, *15* (1986) 1, and references cited therein.