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# Photoreaction of Monochlorobenzene under Ultraviolet Irradiation

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The photolysis of monochlorobenzene by ultraviolet irradiation was investigated and found to yield monochlorinated biphenyls, biphenyl, and benzene. The amounts of these products increased with reaction time up to 20 hours. The yields of 2-, 3- and 4-chlorobiphenyl, biphenyl and benzene in monochlorobenzene were 708 ppm, 965 ppm, 1012 ppm, 226 ppm and 410 ppm, respectively, after 20 hours, but subsequent increases were relatively slow. One possibility is that monochlorinated biphenyls formed from monochlorobenzene are gradually decomposed by further irradiation. The photostability of monochlorinated biphenyls and biphenyl was in the order: biphenyl$\gg$4-chlorobiphenyl$>$3-chlorobiphenyl$>$2-chlorobiphenyl.

**Keywords**——photoreaction; ultraviolet irradiation; monochlorobenzene; monochlorinated biphenyls; polychlorinated terphenyls

Polychlorinated biphenyls (PCBs) were synthesized in 1881 by Schmidt *et al.*[2] have been used for various industrial purposes throughout the world since 1929. In 1970 more than 100000 tons of PCBs were produced in the world, and in Japan approximately 11000 tons were used. Since the first report on PCB contamination in the environment was published by Holden *et al.*[3] in 1967, PCBs have been widely detected not only in aquatic and atmospheric environments but also in biological systems. It has long been well-known that PCB contamination can result from the direct use of PCBs. However, the indirect use of PCBs in industrial compounds must also be considered. Little attention has been given to the presence of PCBs, for example, in industrial chlorinated chemicals. These PCBs do not contain the same components as the PCBs present in the environment.

In connection with these considerations, we have recently shown that chlorobenzenes are converted to PCBs in sunlight[4] and that PCBs are also present in phthalocyanine pigments.[5]

In addition, Augood *et al.*,[6a] Shih *et al.*,[6b] Migita *et al.*[7a] and Ito *et al.*[7b] have reported on the formation of PCBs from monochlorobenzene in the presence of benzoyl peroxide or related radical sources. This paper describes the formation of PCBs from monochlorobenzene and their fate under ultraviolet irradiation.

## Experimental

**Materials**——Monochlorobenzene (MCB), *o*-dichlorobenzene (*o*-DCB), benzene and hexane were purchased from Wako Pure Chemical Industries, Ltd., and their purities were found to be 99.7%, 95.4%, 99.9%

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[1] Location: *2-4-1, Marunouchi, Kochi, 780, Japan.*

[2] H. Schmidt and G. Shultz, *Ann. Chem.*, **207**, 320 (1881).

[3] A.V. Holden and K. Marsden, *Nature* (London), **216**, 1274 (1967).

[4] M. Uyeta, S. Taue, K. Chikasawa, and M. Mazaki, *Nature* (London), **264**, 583 (1976).

[5] M. Uyeta, S. Taue, and K. Chikasawa, *Bull. Environ. Contam. Toxicol.*, **16**, 417 (1976).

[6] *a*) D.R. Augood, D.H. Hey, and G.H. Williams, *J. Chem. Soc.*, **1953**, 44; **1953**, 3412; *b*) C. Shih, D.H. Hey, and G.H. Williams, *ibid.*, **1958**, 2600.

[7] *a*) T. Migita, N. Morikawa, and O. Simamura, *Bull. Chem. Soc. Jpn.*, **36**, 980 (1963); *b*) R. Ito, T. Migita, N. Morikawa, and O. Simamura, *ibid.*, **36**, 985 (1963); **36**, 992 (1963); *idem*, *Tetrahedron*, **21**, 995 (1965).

and 99.9%, respectively, by gas chromatography. Biphenyl (BP) was purchased from Wako Pure Chemical Industries, Ltd., and purified by recrystallization from methanol–water. Gas chromatographic analysis indicated 99.9% purity. 2-Chlorobiphenyl (2-MCBP) was prepared by the Gomberg reaction[8] of 2-chloroaniline with benzene, and purified by distillation *in vacuo*, silica gel column chromatography, and recrystallization from methanol–water. mp 33.5°; bp 118° (0.4 mmHg); UV $\lambda_{\text{max}}^{\text{hexane}}$: 241 nm; IR $\nu_{\text{max}}^{\text{KBr}}$ cm$^{-1}$: 1472, 1078, 1039, 755, 705; MS *m/e*: 190 ($M^+ + 2$), 188 ($M^+$), 153 ($M^+ - Cl$). Gas chromatographic analysis indicated 99.6% purity. 3-Chlorobiphenyl (3-MCBP) was prepared from 3-chloroaniline similarly, and purified by redistillation *in vacuo* and by silica gel column chromatography. bp 126.5—127° (0.4 mmHg); UV $\lambda_{\text{max}}^{\text{hexane}}$: 249 nm; IR $\nu_{\text{max}}^{\text{liq.}}$ cm$^{-1}$: 1596, 1478, 1099, 795, 754; MS *m/e*: 190, 188, 153. Gas chromatographic analysis indicated 99.5% purity. 4-Chlorobiphenyl (4-MCBP) was prepared from 4-chloroaniline similarly, and purified by silica gel column chromatography and by recrystallization from methanol–water. mp 77—77.5°; UV $\lambda_{\text{max}}^{\text{hexane}}$: 253 nm; IR $\nu_{\text{max}}^{\text{KBr}}$ cm$^{-1}$: 1483, 1101, 839, 760, 691; MS *m/e*: 190, 188, 153. Gas chromatographic analysis indicated 99.8% purity.

**UV Irradiation and Analysis of the Products**——The UV irradiation apparatus is shown in Fig. 1. The light source used was a high-pressure mercury lamp (Toshiba SHL-1000 UV-2) with a water-cooled reaction vessel.

MCB (120 ml) was placed in this reaction vessel, and UV irradiation was carried out at 15° for 30 hours. An aliquot of irradiated MCB (2 g) was then placed in a 30 cm × 2 cm (i.d.) column, packed with 20 g of silica gel (Wako gel S-1) activated at 130° for two days. MCB was eluted with 300 ml of hexane, and then PCBs were eluted with 300 ml of methylene chloride/hexane/acetonitrile (80: 19: 1). The PCBs fraction was concentrated to 5 ml, and subjected to column chromatography on 10 g of Florisil activated at 130° for two days, eluting with 200 ml of hexane. The eluate was concentrated to 5 ml and analyzed by GC–MS, as described below.

Furthermore, every two hours during the above irradiation, a 3 ml sample of the irradiated MCB was taken, and the amounts of the photoproducts were determined by GLC as described later. The experiments were carried out three times under the same conditions.

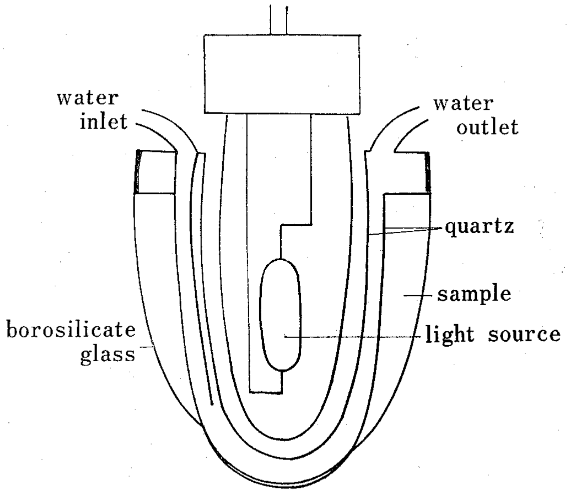

Fig. 1. Apparatus for Ultraviolet Light Irradiation

In order to determine whether monochlorinated biphenyls (MCBPs) further decompose or not during the irradiation, individual MCBP isomers (*ca.* 120 mg each) or mixtures were irradiated for 24 hours in 120 ml of benzene, *o*-DCB or hexane. The yields of BP formed and MCBPs remaining were analyzed by GLC in triplicate.

**Gas–Liquid Chromatography (GLC)**——This was performed with a Shimadzu GC-5A unit equipped with a hydrogen flame ionization detector. A 2 m × 3 mm (i.d.) glass column packed with 25% DEGS on Gaschrom Q (80—100 mesh) was used. The column oven was maintained isothermally at 100° or 180°. The carrier gas was nitrogen.

For analysis of polychlorinated terphenyls (PCTs), a Shimadzu GC-4A unit equipped with a $^{63}$Ni electron capture detector was used. The column was a 1.5 m × 3 mm (i.d.) glass column packed with 1% SE-30 on Gaschrom Q (80—100 mesh). The oven temperature was maintained at 250°. The carrier gas was nitrogen.

**Gas–Liquid Chromatography-Mass Spectrometry (GC–MS)**——GC–MS analysis was carried out with a Shimadzu GCMS-9000 machine at an ionization voltage of 70 eV and accelerating voltage of 3.5 kV. The separation was carried out on a 1.5 m × 3 mm (i.d.) glass column packed with 10% DEGS on Gaschrom W (80—100 mesh).

## Results and Discussion

### Formation of MCBPs, BP and Benzene from MCB on UV Irradiation

Gas chromatograms of the photoproducts formed from MCB are shown in Figs. 2 and 3, and the yields every 2 hours are shown in Fig. 4.

As shown in Figs. 2 and 3, 2-, 3- and 4-MCBP, BP and benzene were formed from MCB under UV irradiation. Each peak on the gas chromatogram was identified by GC–MS, by

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[8] O. Hutzinger, S. Safe, and V. Zitko, *Bull. Environ. Contam. Toxicol.*, **6**, 209 (1971).

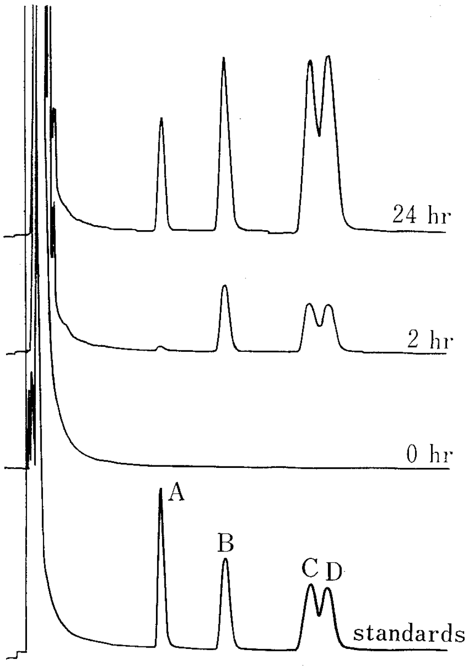

Fig. 2. Gas Chromatograms of MCBPs and BP formed from MCB

A: biphenyl, B: 2-chlorobiphenyl, C: 3-chlorobiphenyl, D: 4-chlorobiphenyl.
Shimadzu GC-5A, FID, 25% DEGS/Gaschrom Q(80—100 mesh), 2 m × 3 mm, 180°.

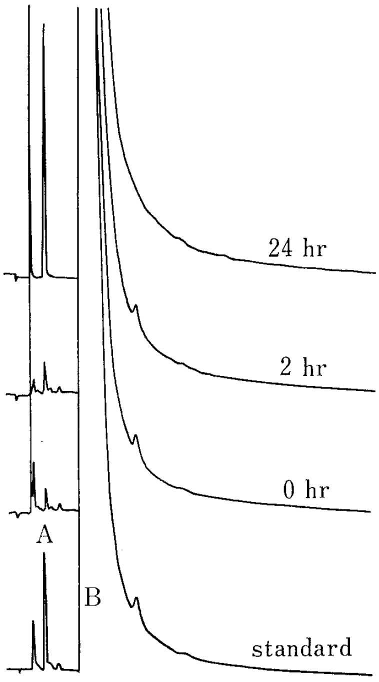

Fig. 3. Gas Chromatograms of Benzene formed from MCB

A: benzene, B: monochlorobenzene. Shimadzu GC-5A, FID, 25% DEGS/Gaschrom Q(80—100 mesh), 2 m × 3 mm, 100°.

comparison with appropriate standards. The amounts of the three MCBP isomers and BP in MCB increased with reaction time as indicated in Fig. 4. After irradiation for 20 hours, the yields of 2-, 3- and 4-MCBP, BP and benzene were found to be 708 ppm, 965 ppm, 1012 ppm, 226 ppm and 410 ppm, respectively. These values corresponded to the yields on outdoor sunlight exposure at our laboratory for 19 months.[9] Slight increases in the yields were still observable on further irradiation. The ratio of 2-MCBP, 3-MCBP and 4-MCBP produced after irradiation for 30 hours was 28: 35: 37. This result is different from those obtained by Shih *et al.*[6b] and Ito *et al.*[7b]

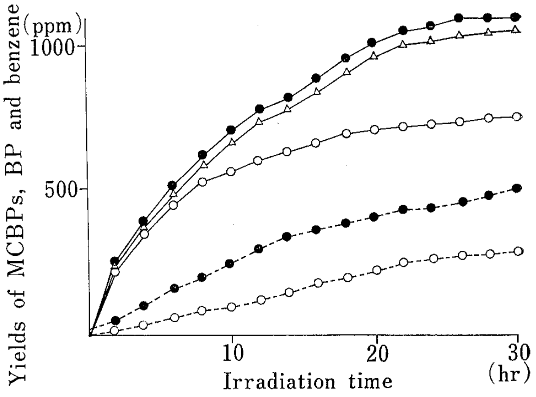

Fig. 4. Photoformation of Monochlorinated Biphenyls, Biphenyl, and Benzene from Monochlorobenzene

—○—: 2-chlorobiphenyl, —△—: 3-chlorobiphenyl, —●—: 4-chlorobiphenyl, --○--: biphenyl, --●--: benzene.
Each point represents a mean of three experiments.

## Photodegradation of MCBPs under UV Irradiation

It was assumed that MCBPs and BP, once formed from MCB, might be decomposed by further irradiation. A sample (120 mg) of each compound was therefore irradiated at 15° in 120 ml of benzene, *o*-DCB or hexane for 24 hours in order to examine its photostability.

Tables I and II show that MCBPs were partly dechlorinated by UV irradiation to form BP, whereas BP was not further decomposed. The rate of dechlorination of MCBPs depended on both the position of chlorine in the benzene ring and the solvent used.

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[9] Unpublished.

TABLE I. Photodegradation of Monochlorinated Biphenyls in Some Organic Solvents

| Solvent | Irradiated MCBP | Conc. (ppm) of MCBP 0 hr | Conc. (ppm) of MCBP 24 hr | Degradation (%) | BP formed from MCBP (ppm) | BP formed/MCBP degraded (mol %)[a] |
|---|---|---|---|---|---|---|
| Benzene | 2-MCBP | 1015 | 509 | 50 | | |
| | 3-MCBP | 1054 | 890 | 16 | 72[b] | 12.7[c] |
| | 4-MCBP | 1058 | 1036 | 2 | | |
| | 2-MCBP | 1008 | 364 | 64 | 86 | 16.3 |
| | 3-MCBP | 987 | 808 | 18 | 8 | 5.4 |
| | 4-MCBP | 1005 | 995 | 1 | 0 | 0 |
| *o*-DCB | 2-MCBP | 991 | 724 | 27 | | |
| | 3-MCBP | 1010 | 916 | 9 | 34[b] | 11.1[c] |
| | 4-MCBP | 1001 | 989 | 1 | | |
| | 2-MCBP | 1020 | 672 | 34 | 47 | 16.5 |
| | 3-MCBP | 959 | 851 | 11 | 5 | 5.6 |
| | 4-MCBP | 989 | 977 | 1 | 0 | 0 |
| Hexane | 2-MCBP | 1088 | 472 | 57 | | |
| | 3-MCBP | 1176 | 937 | 20 | 264[b] | 34.2[c] |
| | 4-MCBP | 1077 | 991 | 8 | | |
| | 2-MCBP | 1069 | 283 | 74 | 299 | 46.4 |
| | 3-MCBP | 1032 | 678 | 34 | 26 | 9.0 |
| | 4-MCBP | 961 | 893 | 7 | 0 | 0 |

*a*) $\text{mol \%} = \frac{\text{BP formed}}{\text{MCBP degraded}} \times \frac{188}{154} \times 100$

*b*) Total yield of BP formed from the three MCBP isomers.

*c*) mol % of BP formed relative to the total amount of the three MCBP isomers degraded.

TABLE II. Photodegradation of Biphenyl in Some Organic Solvents

| Solvent | Irradiated compound | Conc. (ppm) of biphenyl 0 hr | Conc. (ppm) of biphenyl 24 hr |
|---|---|---|---|
| Benzene | Biphenyl | 1000 | 1044 |
| *o*-DCB | Biphenyl | 1000 | 1005 |
| Hexane | Biphenyl | 1500 | 1500 |

Among the three isomers, 4-MCBP had the highest photostability. 2-MCBP was most readily decomposed, and the decomposition amounted to 34 to 74%. The yields of BP formed by photodechlorination of 2-, 3- and 4-MCBP in both *o*-DCB and benzene were 16.4 %, 5.5% and 0%, respectively. However, those in hexane solution were 46.4%, 9.0% and 0%, respectively, indicating readier decomposition of 2- and 3-MCBP in this solvent than in other solvents.

The UV spectra of 2-, 3- and 4-MCBP, and BP in hexane showed absorption maxima at 241, 249, 253 and 258 nm, respectively (the spectral energy distribution of the UV lamp in these regions was flat). Accordingly, the difference in decomposition rates for MCBP isomers is suggested to depend on their photostability, which thus decreases in the following order: BP$\gg$4-MCBP$>$3-MCBP$>$2-MCBP. It can be assumed that a part of the MCBPs produced from MCB under UV irradiation further decomposes gradually on continuing irradiation to yield BP.

### Photoproducts Other than MCBPs, BP and Benzene

The solution of MCB slowly became colored during UV irradiation and eventually turned dark brown. This suggests considerable decomposition of MCB and therefore the photoproducts were analyzed carefully by GLC.

It was found that the reaction mixture contained mono- and dichlorinated terphenyls and HCl in addition to the three MCBP isomers, BP and benzene. The determination of polychlorinated terphenyls (PCTs) was carried out as follows. Irradiated MCB (5 g) was evaporated off using a rotary evaporator. The residue was dissolved in 10 ml of the BMC reagent[10] and the mixture was heated at 65—69° for 4 hours. Tetradecachloroterphenyl formed was analyzed by GLC as described in "Experimental". After irradiation for 30 hours, 73 ppm of PCTs was detected in the resulting solution.

It should also be noted that the content of unidentified products was almost equal to that of MCBPs. They consisted of compounds more polar than PCBs; they were separated by Florisil column chromatography and gel permeation chromatography and analyzed by GC–MS.[11] The results suggested that quaterphenyl, mono- and dichlorinated quaterphenyls, di-, tri-, and tetrachlorinated cyclohexenyl benzenes and triphenylene were present.

Determination of these compounds is in progress and will be reported elsewhere.

**Acknowledgement** We wish to thank Prof. H. Yoshimura, Faculty of Pharmaceutical Sciences, Kyushu University, for his valuable suggestions. Thanks are also due to Mr. S. Takahashi, Shimadzu Seisakusho Ltd. for GC–MS analysis.

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[10] O. Hutzinger, S. Safe, and V. Zitko, *Int. J. Environ. Anal. Chem.*, 2, 95 (1972); Y. Masuda, R. Kagawa, and M. Kuratsune, *J. Food Hyg. Soc. Japan*, **17**, 451 (1976).

[11] Irradiated MCB (500 g) was concentrated in a rotary evaporator. The residue was dissolved in 5 ml of a mixture of hexane/methylene chloride (9: 1), and placed on a 20 g Florisil column, then eluted with 200 ml of hexane (A), 300 ml of methylene chloride (B), and 300 ml of acetone/methanol (1: 1) (C). Eluate B was concentrated to 5 ml, and cleaned up by gel permeation chromatography (HSG-15). The initial eluate (35 ml), which contained compounds more polar than PCBs, was collected and analyzed by GC–MS.