BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (3), 884—887 (1979)

Photoinduced Dechlorination of β-Benzene Hexachloride in Alkaline Alcohols[1]

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(Received August 9, 1978)

Photo-induced dechlorination of β-benzene hexachloride(β-BHC) in alkaline alcohols has been studied. Benzene is a major product accompanying other minor products such as chlorobenzene, alkoxybenzene, and benzyl alcohols. Their yields vary a great deal depending on the kind of alcohol. The efficiency of reaction and the selectivity of benzene increase in the order : methanol<ethanol<2-propanol. The reaction may go by way of dechlorination of β-BHC with base in the dark giving trichlorobenzenes(predominantly 1,2,4-isomer) followed by its photochemical dechlorination. The radical chain mechanism involving H-abstraction by Cl· atom is presented, since the efficiency is raised *ca.* 8 times as much as that in the dark.

Attention has recently been centered upon the photochemical decomposition of organic chlorine-containing compounds as pollutants. Several reports have appeared on the photodechlorination of polychlorinated biphenyl(PCB) in either neutral or alkaline media,[2-8] since PCB has high stability and high resistance against thermolysis.

On the other hand, the photochemical decomposition of aliphatic chlorine-containing compounds used as insecticides, *e.g.*, Aldrin, Deldrin, Endrin or γ-BHC, is difficult on account of their transparency towards UV light over 230 nm,[9,10-12] so that few attempts have been made to decompose the aliphatic chlorine-containing compounds. Only a qualitative study on photoinduced decomposition of γ-BHC with sodium hydroxide in 2-propanol was reported, but no attempt was made for identification of the photoproducts and no mechanistic study carried out.[12]

The present work was undertaken to elucidate photoproducts and to present the mechanism for photoinduced decomposition of β-BHC in various alkaline alcohols.

Results and Discussion

Photodecomposition of β-BHC in Alkaline Alcohols. Irradiation of 0.01 M β-BHC in *ca.* 0.3 M alkaline alcohols with a 300 W high pressure Hg lamp (wavelength 360—600 nm) results in the decomposition of β-BHC with efficiency depending on the kind of alcohol used (Fig. 1). The efficiency increases with the change of alcohol in the order: MeOH<EtOH<2-PrOH. β-BHC is transparent at wave length over 200 nm, but on addition of alkali, a dark reaction occurs forming aromatics, so that the solution absorbs the 270—280 nm light.

The decomposition rate in 2-propanol is *ca.* 8 times as high as that in methanol, all β-BHC being completely consumed within 2 h. However, the yield of benzene still increased even after 100% consumption of β-BHC, reaching a maximum value after 6 h, implying the intervention of precursors to benzene. A slight decrease in the yield of benzene after reaching its maximum can be attributed to further degradation, *e.g.*, benzene reacts with chlorobenzene to give biphenyl.[12]

The extent of dechlorination of β-BHC was estimated to be 4.89 of Cl atoms per one molecule of β-BHC decomposed (or 81% Cl^- production), indicating the formation of chlorine-containing substances in yields of 19% based on the decomposed β-BHC. Most of them could not be identified except for chlorinated benzenes such as mono-, di-, and trichlorobenzenes which appeared in the initial stage of the decomposition of β-BHC.

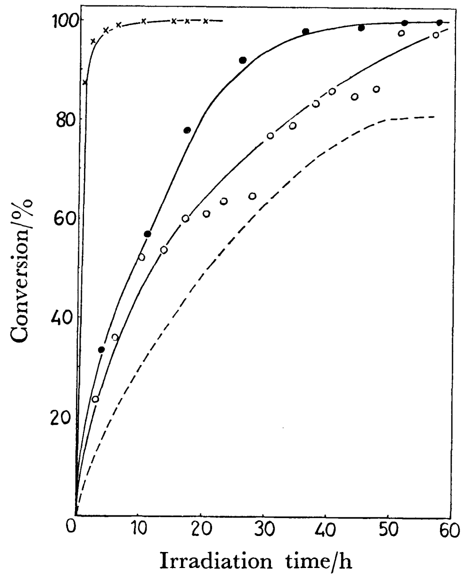


Fig. 1. Irradiation time-conversion curve of photodecomposition of β-BHC in various alkaline alcohols: methanol (—O—O—), ethanol(—●—●—), and 2-propanol(—×—×—). A curve (----) obtained on the basis of chloride ion at 15—20 °C.

Scheme 1 represents the isolated and/or characterized photoproducts in various alkaline alcohols. Their yields after almost complete decomposition of β-BHC are summarized in Table 1.

Products were identified and estimated by means of GLC and GLC-MS in comparison with the corresponding authentic samples.

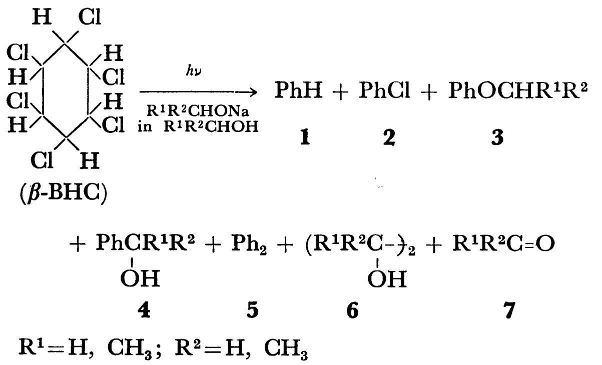
Formation of the corresponding carboxylic acids was observed by further oxidation of **7**'s in an aerated solution. They were characterized as their corresponding esters by addition of excess HCl to the reaction mixture; *e.g.*, methyl formate from formaldehyde.

Benzene was obtained as the major non-chlorine containing product in yields of 23.5, 37, and 48% in alkaline methanol, ethanol, and 2-propanol, re-

Table 1. Products from photolysis of β-BHC in alkaline alcohols[a)]

$[\beta\text{-BHC}]_0$	$[R^1R^2CHONa]_0$ in R^1R^2CHOH	Irrad. time (h)	Conv. (%)	Yield (%) PhH (**1**)	PhCl (**2**)	$PhOCR^1R^2$ (**3**)	$PhCR^1R^2$ OH (**4**)	Ph_2 (**5**)
0.02	0.36 ($R^1=R^2=H$)	50	91	23.6	3.5	2.3	2.3	0.5
0.017	0.28 ($R^1=H$, $R^2=CH_3$)	17	78	21	12.1	3.8	12.3	2.5
0.017	0.28 ($R^1=H$, $R^2=CH_3$)	56	100	37	1.0	—b)	—b)	—b)
0.011	0.19 ($R^1=R^2=CH_3$)	2	96	14	20	—b)	—b)	—b)
0.011	0.19 ($R^1=R^2=CH_3$)	6	100	48	11	—b)	—b)	—b)

a) Conversion and yields were measured by means of GLC using bromobenzene and/or diphenylmethane as internal standard reagents. b) Not determined.



Scheme 1.

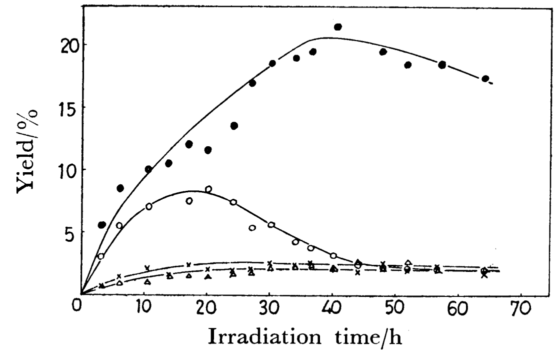


Fig. 2. Irradiation time-conversion curve of photodecomposition of β-BHC to give benzene (—●—●—), chlorobenzene (—O—O—), anisole (—×—×—), and benzyl alcohol (—△—△—) in alkaline methanol at 15—20 °C.

spectively.

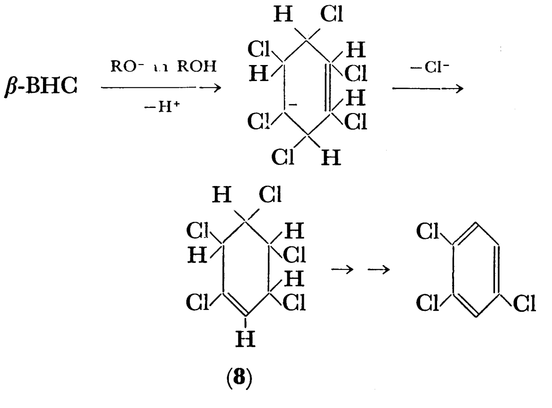
Although 81% of chlorine of β-BHC was liberated as chloride ion, the material balance calculated by means of the chloride formed deviates significantly from that on the basis of cyclic six-membered carbon compounds which comprise benzene, chlorobenzene, alkoxybenzene, benzyl alcohols, and bibenzyl. Total yields of the aromatic compounds are at most as follows: 45.5% for the case in metanol, 50% in ethanol, and 60% in 2-propanol. The loss of Cl content can be attributed to the formation of ring-ruptured chlorine-containing fragments and/or polymerized β-BHC which cannot be detected by GLC up to 250 °C. Detection of fragments or oligomers derived from β-BHC was unsuccessful even by careful GLC analysis.

Effect of Irradiation Time on Photoproducts. A typical example of photolysis of β-BHC in alkaline methanol is shown in Fig. 2. Apparently no substantial amounts of di- and trichlorobenzenes were formed even at the initial stage

Independent photolysis of 1,2,4-trichlorobenzene in alkaline ethanol generated 74% of chloride ion. It is assumed that three atoms of chlorine are liberated from one molecule of the trichlorobenzene, thus yielding benzene, chlorobenzene and phenetole (33, 45, and 22%, respectively).

Competitive dechlorination with a mixture of 1,2,4-trichloro-, 1,2-dichloro-, 1,4-dichloro-, and monochlorobenzenes showed that the 1,2,4-isomer is the most unstable towards UV light and monochlorobenzene the most stable; 1,2,4- and 1,2-halides are almost photodecomposed within 1.5 h irradiation, whereas the mono- and 1,4-dihalides require over 6 h for almost complete decomposition. This suggests that the trichlorobenzene is formed at the earliest stage, but it does not accumulate on account of its instability towards UV light in the presence of alkali.

Progressive Dechlorination of β-BHC. β-BHC is stable under UV irradiation because of its transparency to UV light over 230 nm. The initiation



(**8**)

(1)

necessitates UV-absorbing species. Trichlorobenzenes containing 87% of the 1,2,4-isomer are formed in the dark by treatment of β-BHC in alkaline methanol.[13] The reaction is explained by a mechanism involving a carbanion formed by deprotonation of β-BHC with alkoxide.[13] Trichlorobenzenes, however, do not undergo dechlorination with alkali in the dark, but they are easily decomposed into benzene, chlorobenzene, and alkoxybenzene on irradiation as described above.

Hence, the photolysis of β-BHC is apparently initiated by the trichlorobenzenes. Nevertheless, the photoinduced dechlorination of β-BHC cannot be explained only by the photodecomposition of trichlorobenzenes, since the photoinduced decomposition of β-BHC is *ca.* 8 times as fast as that in the dark (Fig. 3).

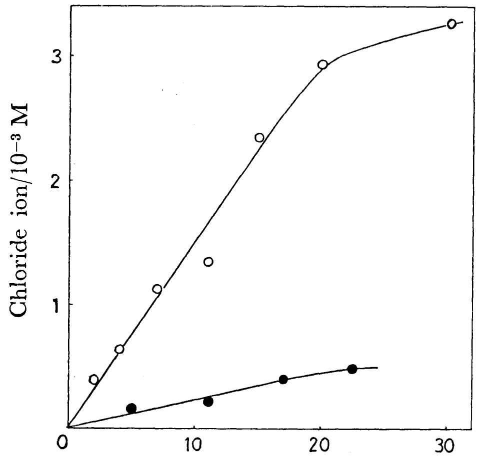


Fig. 3. The time dependence of the formation of chloride ion at 25 °C (a) on photolysis of an ethanol solution of β-BHC (0.0014 M) and sodium hydroxide (0.028 M) (—○—○—) and (b) on standing it in the dark (—●—●—) at 15—20 °C.

If only the above carbanionic dechlorination of β-BHC with alkali is operating, the efficiency of photoinduced consumption of β-BHC would not exceed that in the dark. A radical chain mechanism is conceivable in which dechlorination of β-BHC occurs mainly via a hydrogen abstraction by chlorine atom generated by photolysis of trichlorobenzenes.

$$\beta\text{-}C_6H_6Cl_6 + 3RO^- \xrightarrow[\text{dark}]{\text{ROH}} C_6H_3Cl_3 + 3ROH + 3Cl^- \qquad (2)$$

$$C_6H_3Cl_3 \xrightarrow{h\nu} C_6H_3Cl_2\cdot + \cdot Cl \qquad (3)$$

$$Cl\cdot + \beta\text{-}C_6H_6Cl_6 \longrightarrow HCl + C_6H_5Cl_6\cdot \qquad (4)$$

$$\underset{(\mathbf{8})}{C_6H_5Cl_6\cdot} \longrightarrow C_6H_5Cl_5 + Cl\cdot \qquad (5)$$

$$\mathbf{8} \longrightarrow C_6H_3Cl_3 + 2HCl \qquad (6)$$

$$C_6H_3Cl_2\cdot + R^1R^2CHOH \longrightarrow C_6H_4Cl_2 + R^1R^2\underset{\cdot}{C}OH \qquad (7)$$

$$R^1R^2\underset{\cdot}{C}OH + Cl\cdot \longrightarrow R^1R^2C{=}O + HCl \qquad (8)$$

$$2R^1R^2\underset{\cdot}{C}OH \longrightarrow \underset{\text{(pinacol)}}{(R^1R^2\underset{\text{OH}}{\underset{|}{C}}\text{-})_2} \qquad (9)$$

Analogously,

$$C_6H_4Cl_2 + R^1R^2CHOH \xrightarrow{h\nu} C_6H_5Cl + R^1R^2\underset{\cdot}{C}OH + Cl\cdot \qquad (10)$$

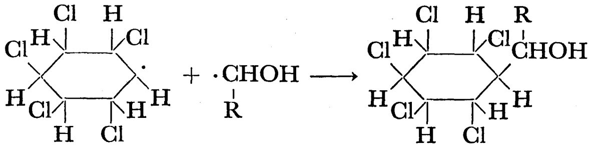
$$C_6H_5Cl + R^1R^2CHOH \xrightarrow{h\nu} C_6H_6 + R^1R^2\underset{\cdot}{C}OH + Cl\cdot \qquad (11)$$

Pinacol was accumulated during the course of irradiation, especially in 2-propanol, 2,3-butanediol being rapidly accumulated even after 100% decomposition of β-BHC. The pinacol is derived by photoreduction of acetone in 2-propanol. The formation of biphenyl is explained by the reaction of chlorobenzene with benzene.

$$C_6H_5Cl + C_6H_6 \xrightarrow{h\nu} Ph_2 + HCl \qquad (12)^{12)}$$

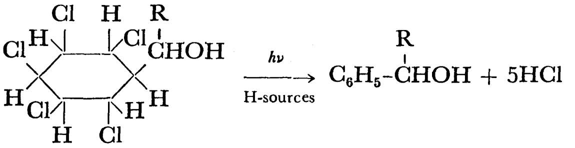
Chlorobenzene is known to be easily photodecomposed to give alkoxybenzene or phenol by photosubstitution along with benzene.[14–17] In our photoreaction, anisole (in methanol) and phenetole (in ethanol) were observed (see Table 1). However, careful analysis by GLC and GLC-MS revealed no formation of tri- or dialkoxybenzenes, and/or alkoxychlorobenzenes, suggesting that tri- or dichlorobenzenes are very rapidly dechlorinated rather than undergoing nucleophilic substitution under these conditions.

It is of interest that aromatic radical substitution occurs; *i.e.*, benzyl alcohol and 1-phenylethanol are formed during photolysis. Independent photolysis of trichlorobenzenes, or chlorobenzene under similar conditions did not afford such products; hence the substitution may originate at the stage of dechlorination of β-BHC. They may be formed as follows.



(13)

(R=H, or CH_3)



$$\xrightarrow[\text{H-sources}]{h\nu} C_6H_5\text{-}\overset{R}{\overset{|}{C}}HOH + 5HCl \qquad (14)$$

This is an evidence for the homolytic dechlorination of β-BHC to the radical $\cdot C_6H_6Cl_5$ through a radical chain mechanism involving chlorine atom as a chain carrier.

Experimental

Materials. β-BHC(extra pure grade, Tokyo Kasei Co.) was used without further purification. 2,3-Butanediol was synthesized by photolysis of acetone in 2-propanol.[18] *o*-(and *p*-)Chlorophenetoles were prepared by treatment of *o*-(and *p*-)chlorophenols with ethyl bromide in the presence of potassium carbonate.[19]

General Procedures. A Halos high-pressure 300 W Hg lamp with a water-cooling quartz jacket was used as a light source immersed in a reaction solution in a reactor (1000 ml volume) equipped with a thermometer and a condenser. The reaction solution was adjusted to contain 0.01 M β-BHC and 0.3 M sodium alkoxide in alcohol. The reaction mixture was irradiated until the starting β-BHC disappeared. Aliquots were taken out at appropriate intervals of time, yields being estimated by means of titration and GLC technique.

Analysis of Products. Identification of products was carried out by means of GLC with a Yanagimoto gas chromatograph, Model GCG-550F operated with columns packed with either PEG 20 M (4 mm×1.2 m) or Porapak QS (4 mm×0.7 m) using N_2 as a carrier gas. Low-boiling products such as benzene, chlorobenzene, aldehyde, and esters were identified and estimated by means of GLC with a Porapak QS column using bromobenzene as an internal standard in comparison with the corresponding authentic specimen. High-boiling products such as polychlorobenzenes (*e.g.*, 1,2,4-trichlorobenzene), alkoxybenzene, benzyl alcohol, 1-phenylethanol, and β-BHC were identified and estimated by GLC with the PEG 20 M column using diphenylmethane as an internal standard.

The other products such as 1,2-ethanediol were characterized by means of GLC-MS with a Shimadzu GLC-MS Model 7000 as follows : *m/e* (relative yield); benzene, 78(M^+) (100); methyl formate, 60(M^+) (56), 32(100), 31(100); methyl acetate, 74(M^+) (32), 43(100); acetic acid, 60(M^+) (100), 58(13), 44(100), 43(15), 31(100), 32(69), 33(28); benzyl alcohol, 108(M^+) (100), 107(33), 79(50); ethylene glycol, 60(M^+) (25), 45(5), 44(12), 43(10), 33(75), 32(12), 31(100); 1-phenylethanol, 122(M^+) (66), 108(10), 107(100), 79(56), 78(12); butanediol, 90(M^+) (9), 75(10), 68(12), 47(12), 46(8), 45(100), 44(8), 43(8); benzene, 78(M^+) (100); chlorobenzene, 113(M^++1) (30), 112(M^+) (100), 77(45), 51(10), 50(10).

The analysis of chloride ion was carried out by addition of excess silver nitrate (10 ml×0.016 M) to the above aliquot (10 ml), followed by titration with aqueous thiocyanate (0.016 M) after acidification by addition of excess nitric acid. The concentration of the appropriate sodium alkoxide was measured with 0.0662 M HCl using phenolphthalein as an indicator. A control experiment indicated that the covalent-bonded chlorine cannot be detected as chloride ion in the stage of titration.

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