

[報 文]

Photosensitization of Trichlorobenzenes (TCBs) in Aqueous Solution: III. Photoproducts with Nitrite (NO_2) and Triethylamine (TEA)

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ABSTRACT

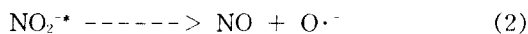
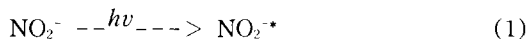
Photolysis of TCBs in aqueous solutions of sodium nitrite and triethylamine (TEA) at neutral pH has been investigated. TCBs yielded trichloronitrobenzenes (TCNBs) as primary photoproducts, and their corresponding trichlorophenols (TCPs) via two types of reaction, one, nitration, and the other, by direct hydroxylation with OH radical. Isomerized products and TCBs were also identified. Photosensitization with TEA resulted in the formation of small yields of dichlorobenzenes (DCBs) by reductive dechlorination of TCBs.

INTRODUCTION

The concern for environmental contamination by TCBs in recent years has prompted efforts to degrade these compounds artificially or naturally in a safe manner. Although some studies have been conducted on photodegradation of TCB in nitrite (NO_2) or TEA aqueous solution, very little definitive work has appeared on the mechanism of the degradation of TCBs with these compounds as photosensitizers. It is well established that the phototransformation of nitrite ions leads to the formation of hydroxyl radical and nitration reaction, indicating that NO_2 is very effective in forming nitrophenol products in solution.^{1, 2)} Several amines such as TEA,³⁾ diisopropylamine,⁴⁾ proteins,⁵⁾ and secondary and tertiary amines⁶⁾ have been previously used to enhance photodegradation of chlorinated aromatic com-

pounds. The dechlorination of aryl chlorides by amine via electron transfer to the aryl halide, takes place mainly from the triplet state.⁷⁾ Alternatively, either singlet or triplet can react with an electron rich donor to produce an exciplex resulting in the C-Cl bond homolysis of aryl radical. Here we examine the effect of NO_2 as an oxidizing agent or electron acceptor, and TEA as a reducing agent or electron donor in the aqueous on the process of photosensitization of the TCBs. Plausible pathways are postulated in this study, and they provide a reasonable framework for discussion of research findings on the degradation procedures.

Nitrite. A number of studies reported that hydroxyl radicals have been generated from nitrite ions⁸⁻¹¹⁾ in aquatic medium as shown by the following primary photochemical process [Eq. (1)-(4)].



The influence of NO_2 on the photochemical reactions of xenobiotics in an aquatic environment has received little attention. It is believed that in aqueous solutions NO_2 undergoes mainly addition reactions to aromatic compounds. The postulation of the mechanism of photochemical formation of phenols from nitro compounds has been shown.^(12, 13) Photolysis of nitrobenzene leads to an excitation state, $^1(n, \pi^*)$ which is the overlap of the half-vacant nonbonding p atomic orbital of oxygen of the nitro-group with the adjacent orbital of the aromatic ring. This overlap, which is the result of the out-of-plane nitro group at right angles (66° – 90° in solution) to the plane of the mesityl ring, leads to the formation of an oxaziridine ring which collapses to the nitrite. The resulting aryl nitrite is very labile and is hydrolyzed to yield the corresponding phenol.⁽¹³⁾

The reaction mechanism undergo radical nitration of aromatics directly by NO_2^{\cdot} generated via thermal, photolytic, or radiolytic ways. These nitrations are characterized as free-radical nitrations.⁽¹⁴⁾

In aqueous solutions, nitrite successfully undergoes nitration, dechlorination, photosubstitution through a free radical or ionic mechanism with highly chlorinated benzenes.^(15, 16) Parlar and their coworkers⁽¹⁷⁾ have reported the aqueous phase photochemical ($254 \text{ nm} \geq \lambda$) reductive dechlorination of dichlorobenzene containing one substituent such as NO_2 . Similar reactions have been observed in the gas phase.⁽¹⁸⁾

Triethylamine (TEA). It is generally accepted that chlorinated aromatics undergo photo-

chemical electron-transfer reactions in the presence of amines.⁽¹⁹⁻²⁰⁾ The influence of amines on the photoreduction of chlorobenzenes,⁽²¹⁾ chlorinated biphenyls⁽²²⁻²⁵⁾ and chloronaphthalene⁽²⁶⁾ have been reported. Amine-assisted photolysis of halobenzenes involves the intermediate of an excited-state charge transfer complex (exciplex) that has been shown in the reaction with chlorinated aromatic compounds involved in the photoprocesses.⁽²⁶⁻²⁸⁾ Alternatively, either the singlet (at higher amine concentrations) or triplet (at lower amine concentrations) can react with an electron-rich donor molecule (amine) to produce an exciplex or radical anion/radical cation ion pair. Hence the addition of amines to polar solvents leads to enhanced dechlorination of the chlorinated aromatic compound. More recently, 1, 2, 3- and 1, 2, 4-TCB were observed to undergo two modes of photodechlorination,⁽³¹⁾ via either (i) bond fission to produce aryl radical and chloride ion or (ii) bond fission to form an aryl carbanion and chloride atom, in acetonitrile with TEA. However, 1, 3, 5-TCB was not dechlorinated.

In this paper, we present the results of the photosensitization of TCBs by NO_2 via photo-oxidation and TEA through reductive dechlorination, isomerization and other reactions also occur, leading to the formation of various photoproducts. We have identified the photoproducts, and examined the reaction mechanisms of nitrations by nitrite (NO_2^-) and the dechlorination mechanism by TEA.

EXPERIMENTAL METHODS

Aqueous concentrations of TEA ($1.5 \times 10^{-3} \text{ M}$) and sodium nitrite ($3.97 \times 10^{-4} \text{ M}$) were added to individual stock solutions of TCBs in dark 1 L bottles and stirred for 10 min in the dark before transferring to test tubes to be used for the exposure experiments. The concentra-

tions of the stock solutions of 1, 2, 3-TCB were 1.59×10^{-4} M, 1.37×10^{-4} M for 1, 2, 4-TCB and 3.30×10^{-5} M for 1, 3, 5-TCB. Sample and reagent preparation and exposure procedures have been previously described.²⁹⁾

RESULTS AND DISCUSSION

I. Photoproducts Formation with Nitrite

1) Photoproducts of 1, 2, 3-TCB

In Fig. 1, it is shown that 2, 3, 4-trichlorophenol (peak 4) and 1, 2, 3-trichloro-5-nitrobenzene (TCNB, peak 7) were predominantly produced during the reaction of 1, 2, 3-TCB in nitrite solution. The trichloronitrobenzene peak was tentatively determined as a *meta* substituted TCNB. It is believed that the activation of the meta position of 1, 2, 3-TCB by NO_2 , an electron withdrawing group, must have a preference since NO_2 is a meta activating group on the benzene ring. NO_2 is known to be eight times stronger as an electron withdrawing group than the Cl atom.³⁰⁾ As

the reaction proceeds, it is observed that the nitroderivative is the primary product formed. In addition to two main photoproducts, small peaks of 1, 2, 3-trichloro-4-nitrobenzene (peak 5) and 3, 4, 5-trichlorophenol (peak 6) appeared at retention times of 18.00 and 18.18 min respectively on the chromatogram.

Small yields of the 3, 4, 5-TCP is also believed to result from the direct hydroxylation on meta-position. In the control samples TCNBs were not found with any TCB isomers, suggesting that TCBs do not react with nitrite solution in the dark. The formation mechanism can be explained by the stereochemistry of TCBs as well as the behavior of NO_2 substituted benzene. The irradiation of 1, 2, 3-TCB in the presence of nitrite brings about nitration to give 1, 2, 3-TC-5-NB as the initial product.

2) Photosensitization of 1, 2, 4-TCB with NO_2

In a previous study,²⁹⁾ it was hypothesized

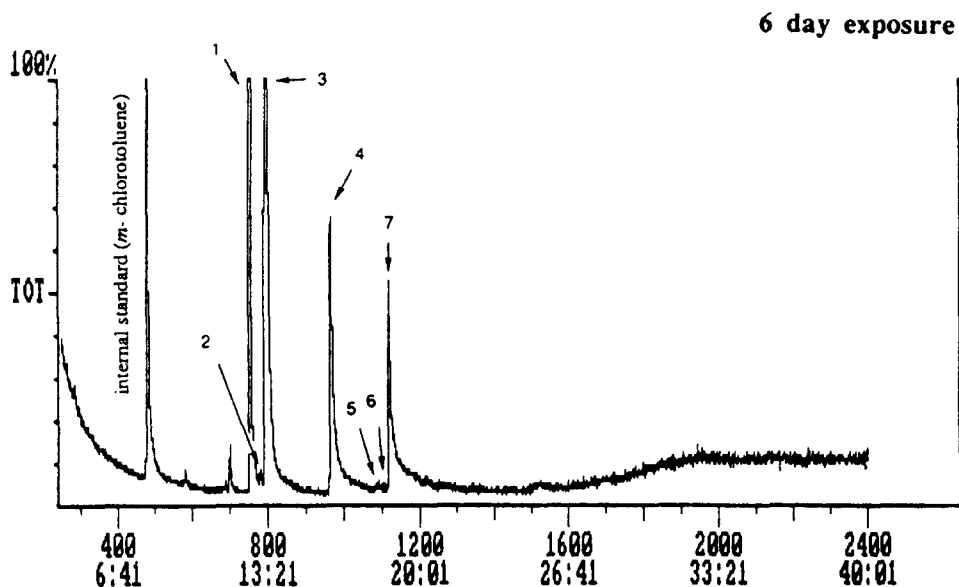


Fig. 1. Total ion chromatogram of the photolyzed 1, 2, 3-TCB in the presence of nitrite after 6-Day Exposure (Experiment 2).

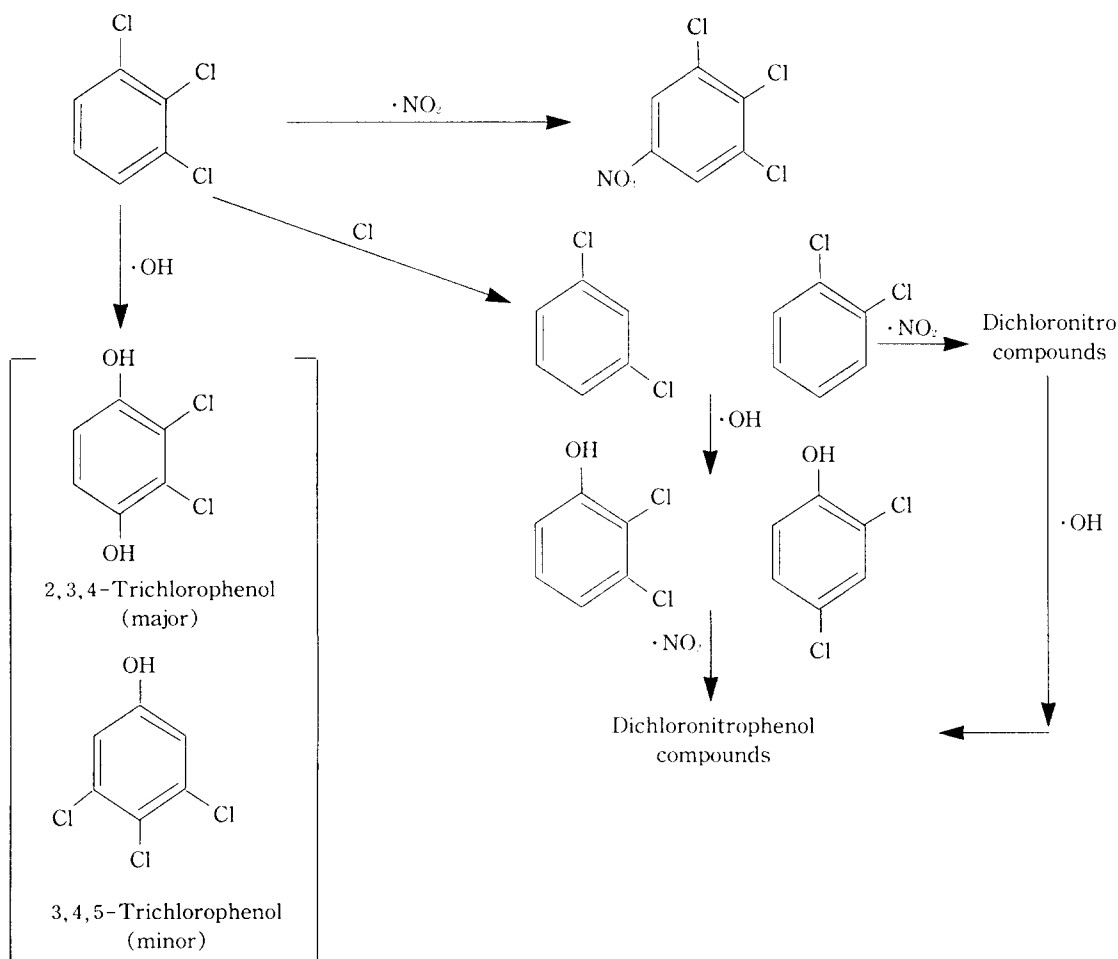


Fig. 2. Postulated reaction mechanism of 1, 2, 3-TCB with nitrite to yield the proposed 1, 2, 3-trichloro-5-nitrobenzene and 2, 3, 4-TCP and 3, 4, 5-TCP via nitration.

that TCPs should be major products of TCBS if OH radicals from Fenton's reagent solution efficiently contribute to produce TCPs from 1, 2, 4-TCB. In the study, it was observed that 1, 2, 4-TCB was not reactive enough to be hydroxylated to produce TCPs in Fenton's reagent. However the nitrite anions appear to efficiently facilitate to add OH radicals between Cl atoms. Peaks [1]-[4] of the phenol products shown in the chromatogram (Fig. 3) were identified by GC/MS. Peaks after 12.35 min were those of TCNBs (between 18 min

and 20 min) and their corresponding TCPs (between 15 min and 17 min). Two distinctive TCNBs were found (expanded part) in the chromatogram. Considering the significant difference of peak areas among TCPs and TCNBs, 3- and 6-positions were highly favored for the nitration of 1, 2, 4-TCB by comparison of the peak area of TCNB even though the peaks were not identifiable because of the unavailability of standard samples. The transformed products of TCNBs were evidently 2, 3, 5-, 2, 4, 5- and 2, 3, 6-TCPs,

but their corresponding 1, 2, 4-TC-6-NB, 1, 2, 4-TC-3-NB except 1, 2, 4-TC-5-NB are tentatively proposed because authentic standards are unavailable. A small peak of 2, 3, 4-TCP (peak 2) at 16.12 min is shown to be close to 2, 4, 5-TCP. Likewise, three different TCPs directly formed from 3 different 1, 2, 4-TCNBs which are formed by addition reaction of OH radical either on 3, 5, and 6 position of 1, 2, 4-TCB or on meta-position of the photoisomer, 1, 2, 3-TCB, were observed. It is possible that the major quantitative photolysis route is via the 3-position, whose peak at 17.88 min appears to be highly selective in the production of 1, 2, 4-TC-3-NB as a major pathway since a high yield of its corresponding 2, 3, 6-TCP is expected to be produced by a fast reaction. The fact that a trace amount of 1, 2, 4-TC-5-NB (peak 6) is shown at 18.30 min in the chromatogram could be explained by assuming that nitration on position 5 is unlikely to occur. Interestingly, the three TCPs photoproducts (2, 3, 5-TCP, 2, 4, 5-TCP and 2, 3, 6-TCP) transfor-

med from their corresponding TCBs yielded the mole ratio of 1:2:5 approximately. The evidence that formation of three noticeable TCPs at 15.34 min, 15.58 min, and a high peak at 16.26 min of retention time gives a reasonable explanation that hydroxylation is expected to vary on the basis of the steric factors such as position, number of chlorine atom substituents in benzene ring or solubility. At the retention time of 16.02 min, a small peak 3 was identified as 2, 3, 4-TCP. The peak at 13.16 min indicates the presence of the photoisomerized 1, 2, 3-TCB from the parent compound, 1, 2, 4-TCB.

Fig. 3. shows the GC/MS chromatogram of the photolyzed 1, 2, 4-TCB in nitrite solution.

3) Photosensitization of 1, 3, 5-TCB with NO₂

Fig. 4 shows the GC/MS chromatogram of the photolyzed 1, 3, 5-TCB in nitrite solution.

The results indicate that unsubstituted 2-, 4- or 6-position of 1, 3, 5-TCB and 3, 5 and 6-position of 1, 2, 4-TCB are very susceptible to NO₂ attack in spite of plausible steric

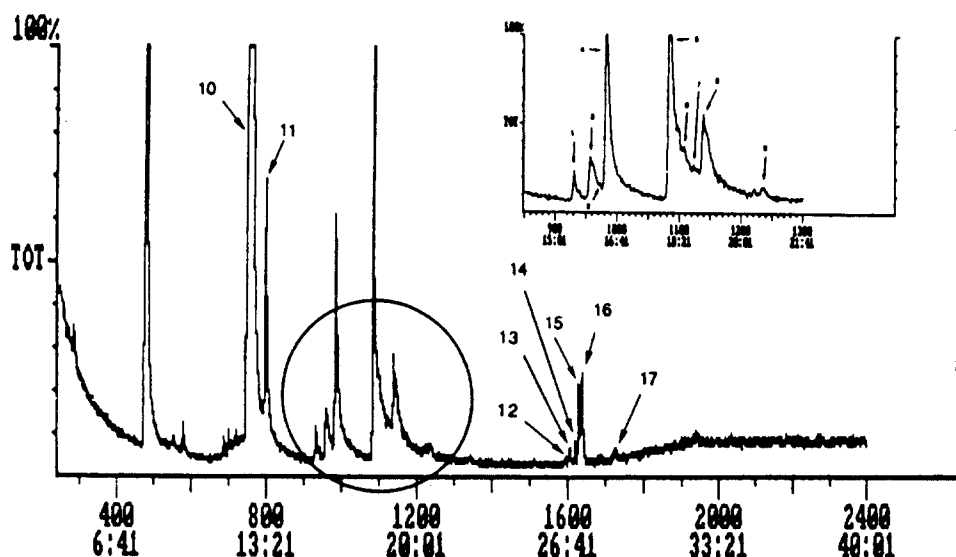


Fig. 3. Total ion chromatogram of the photolyzed 1, 2, 4-TCB in the presence of nitrite after 6-day exposure (Experiment 2).

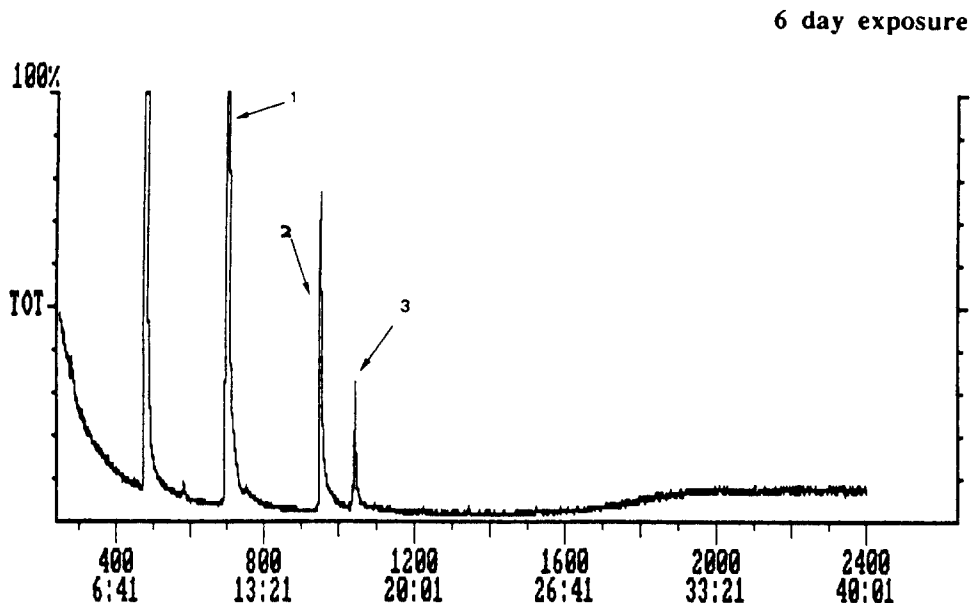


Fig. 4. Total ion chromatogram of the photolyzed 1, 3, 5-TCB in the presence of nitrite after 6-day exposure (Experiment 2).

hindrance by adjacent Cl atoms. A possible explanation is that NO_2 attacks at a distance (coplanar or near 90° angle) from two Cl atoms on both sides and then NO_2 or, both NO_2 and Cl atoms must rotate out of plane to minimize the unfavorable nonbonded contact. This explanation also rationalizes the assumption that the 3-position of 1, 2, 4-TCB is vulnerable to NO_2 addition. It appears that the hydrogen between two adjacent Cl atoms are released by inductive effect and then substituted by a strong electron-withdrawing group, NO_2 . The result also indicates that TCNBs derived from 1, 2, 4- are more reactive than that of 1, 2, 3- or 1, 3, 5-TCB, possibly due to the fact that (i) 1, 2, 3-trichloro-5-nitro-benzene product cannot undergo dechlorination because NO_2 on meta-position is too far from Cl atoms to withdraw electrons to dechlorinate Cl atoms; (ii) 2, 4, 6-TCNB has a stable symmetrical structure that minimizes the activity (polarity) of the

compound. An experiment was demonstrated with exposure of TCNBs only in a vessel if the dechlorination occurs during same exposure time. The result showed no dechlorinated products.

As a result, observations give support to the following pathways of dechlorination mechanism: The reaction route leading to dichlorophenol production most probably involves, (i) the Cl bond cleavage from TCBs may involve reductive dechlorination (ii) a direct addition of hydroxyl ion on DCBs which are directly produced photochemically from TCBs.

The high yield of a dichloronitrophenol was observed from the photolysis of 1, 2, 3-TCB in nitrite solution (Experiment 1). The presence of intense peaks indicating dichloronitrophenol photoproducts proves that irradiation of TCB resulted in the formation of a dichlorophenol and a dichloronitrophenol via dechlorination of TCB to DCB and then the subseq-

uent addition of OH. More dechlorinated products produced in 1, 2, 3-TCB photolysis samples suggest that these products are probably due to the reductive dechlorination of TCBS at shorter wavelengths (Experiment 1).

During the photolysis Experiment 1 using sun lamps, dehalogenation products are also formed. Photolysis of TCB in nitrite solution led to TCNB. Photoexcited TCB undergoes homolytic scission of a C-Cl bond to provide dichloronitrophenyl radicals. The resulting aryl radical reacts with hydrogen taken from

aqueous solvent system and the nitrite on the benzene ring transforms into hydroxide. Formation of further occurs by the addition reaction of nitrite, which would also be hydroxylated on the benzene ring. The same pattern of reactions for the mechanism are followed with 1, 2, 3- or 1, 3, 5-TCB.

Interestingly, a small amount of trichlorobenzenamine was detected during the photolysis of 1, 2, 4-TCB in nitrite solution, indicating that reduction occurred through the addition of hydrogen. Aromatic nitro compounds³¹⁾

Table 1. Summary of identified and proposed photoproducts of TCBS with nitrite (6 day photolysis based on 12hr exposure).

Experiment 1 (sun lamp)		Experiment 2 (black lamp)	
1, 2, 3-TCB	(15.02)	1, 2, 3-TCB	(13.20) [3]
1, 2-dichlorobenzene	(9.08)	1, 2, 4-trichlorobenzene	(12.29) [1]
1, 2, 4-trichlorobenzene	(13.65)	2, 6-dichlorophenol	(12.97) [2]
2, 4-dichlorophenol	(13.70)	2, 3, 4-trichlorophenol	(16.08) [4]
2, 3, 4-trichlorophenol	(20.11)	1, 2, 3-trichloro-5-nitrobenzene	(18.62) [5]*
1, 2, 3-trichloro-5-nitrobenzene	(24.94)*	3, 4, 5-trichlorophenol	(18.18) [6]*
2, 6-dichloro-4-nitriphenol	(27.33)	1, 2, 3-trichloro-5-nitrobenzene	(18.62) [7]*
3, 4, 5-trichlorophenol	(28.24)*		
1, 2, 4-TCB	(13.82)	1, 2, 4-TCB	(13.16) [10]
1, 3-dichlorobenzene	(8.43)	1, 2, 3-TCB	(13.22) [11]
1, 2, 3-trichlorobenzene	(14.84)	2, 3, 5-trichlorophenol	(15.34) [1]
2, 3, 5-trichlorophenol	(18.93)	2, 4, 5-trichlorophenol	(15.58) [2]
2, 4, 6-trichlorophenol	(19.76)	2, 3, 4-trichlorophenol	(16.12) [3]
1, 2, 4-trichloro-3-nitrobenzene	(23.79)	2, 3, 6-trichlorophenol	(16.26) [4]
2, 6-dichloro-4-nitrobenzene	(23.98)*	1, 2, 4-trichloro-3-nitrobenzene	(17.88) [5]*
		1, 2, 4-trichloro-5-nitrobenzene	(18.30) [6]
		1, 2, 3-trichloro-5-nitrobenzene	(19.03) [7]
		1, 2, 4-trichloro-6-nitrobenzene	(19.17) [8]*
		trichlorobenzamine	(20.47) [9]*
		pentachlorobiphenyl	(26.36) [12]*
		pentachlorobiphenyl	(27.10) [13]*
		pentachlorobiphenyl	(27.18) [14]
		pentachlorobiphenyl	(27.28) [15]*
		pentachlorobiphenyl	(28.46) [16]*
1, 3, 5-trichlorobenzene	(12.37)	1, 3, 5-TCB	(11.30) [1]
2, 5-cyclohexadiene-1, 4-dione,		2, 4, 6-trichlorophenol	(15.81) [2]
2, 6-dichloro	(15.35)*	2, 4, 6-trichloro-nitrobenzene	(17.35) [3]
2, 4, 6-trichlorophenol	(19.57)		
2, 4-dichloro-5-nitrophenol	(22.44)*		
2, 6-dichloro-4-nitrophenol	(27.33)		

The figures in () and number in [] indicate retention times of products and number of peaks shown in chromatograms. * represents tentatively proposed photoproducts due to the standard samples unavailable.

and chloronitroaromatic compound³²⁾ in aqueous-alcoholic solution at high pH were converted into aniline derivatives and chloroaniline respectively by the photochemical reduction of the nitrite anion to ammonia upon irradiation. A photochemical reduction of 2,6-DCNB to dichlorobenzenamine was also observed.³³⁾

It is evident that electron withdrawing groups such as nitrite, prompt the isomerization of TCBs. As indicated in the chromatograms, fast isomerization reactions occurred between 1,2,3-TCB and 1,2,4-TCB, observing that 1,2,3-TCB tends to isomerize into 1,2,4-TCB much faster than its reversible reaction. Whereas, slow isomerization was observed between 1,2,4-TCB and 1,3,5-TCB. There was no significant increase of the isomer peak area between the photolyzed sample and dark control.

TCBs in nitrite solution undergo formation

of trichlorophenols (TCPs). Some of the photoproducts also formed include trichloronitrobenzenes (TCNBs) and dichlorophenols (Table 1).

2. Photoproducts Formation on Photolysis of TCBs in TEA Solution

The reaction of TEA with 1,2,3-TCB was believed to occur by electron transfer and was studied during exposure with black lamps and a sun lamp. Both 1,2,3-TCB and 1,2,4-TCB gave dechlorinated photoproducts. 1,3,5-TCB, on the other hand, was found to be less reactive with TEA, and gave 1,3-dichlorobenzene (DCB).

A summary of the identified photoproducts resulting from the photosensitization of TCBs with TEA is shown in Table 2.

It appears that 1,3,5-TCB was too stable to produce dechlorinated photoproducts and that it dechlorinates upon exposure to shorter

Table 2. Summary of identified and proposed photoproducts of TCBs with TEA (6 day photolysis).

Experiment 1 (sun lamp)		Experiment 2 (black lamp)	
1,2,3-TCB		1,2,3-TCB	(13.16) [2]
1,2-dichlorobenzene	(8.25)	1,3-trichlorobenzene	(9.08) [1]
1,3-dichlorobenzene	(8.43)		
1,4-dichlorobenzene	(9.08)		
1,3,5-trichlorobenzene	(13.67)		
1,2,3-trichlorobenzene	(15.25)		
1,2,4-TCB		1,2,4-TCB	(12.33)
1,3-dichlorobenzene	(8.44)	1,3-dichlorobenzene	(9.05) [≠]
1,4-dichlorobenzene	(8.73)	1,4-dichlorobenzene	(9.15) [1]
1,3,5-trichlorobenzene	(13.81)	1,2-dichlorobenzene	(9.62) [2]
1,2,4-trichlorobenzene	(14.84)	pentachlorobiphenyl	(26.73) [5]*
1,2,3-trichlorobenzene	(15.21)	pentachlorobiphenyl	(27.17) [5]*
1,1'-biphenyl, 2,3,3',4,4'-pentachloro	(37.95)*		
1,3,5-TCB		1,3,5-TCB	(11.28)
1,3-dichlorobenzene	(8.44)	no products	
1,3,5-trichlorobenzene	(12.44)		
1,2,4-trichlorobenzene	(13.70)		
1,2,3-trichlorobenzene	(15.02)		

[≠] : represents negligibly small yield. The figures in () and number in [] indicate retention times of products and number of peaks shown in chromatograms. * represents proposed photoproducts due to the standard samples unavailable.

wavelength or with stronger light intensity such as the sun lamp rather than exposure to black lamp. The photosensitization with TEA of 1, 2, 3-TCB gave 1, 3- and 1, 2-DCB with percent ratio of 30%:70%; 1, 4- and 1, 2-TCB with 1, 2, 4-TCB with the ratio of 40%:60%.

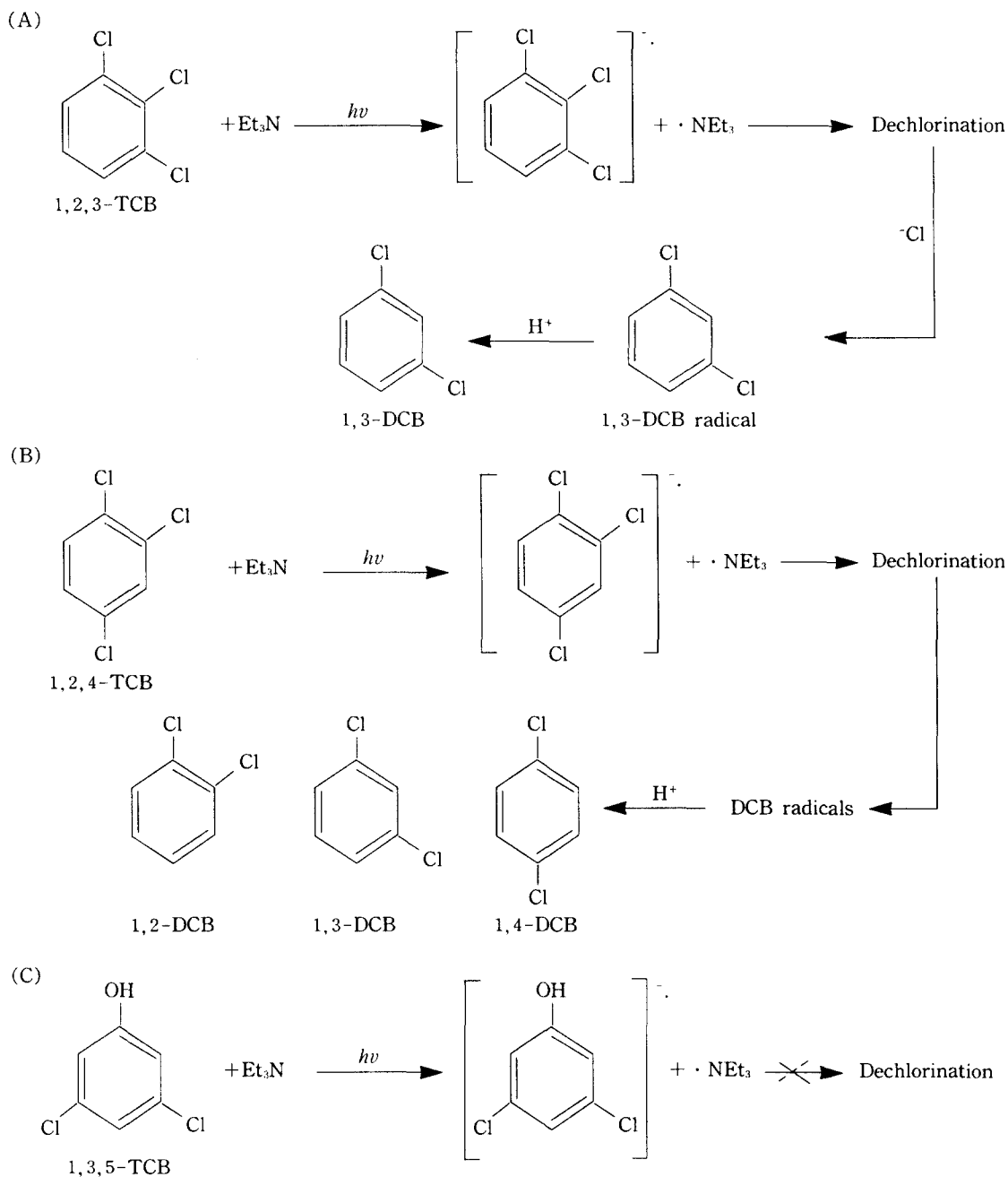


Fig. 5. Photoreaction pathways and photoproducts of TCBS in TEA solution (Experiment 2).

It was reported that TCBS were dechlorinated during photoreaction with TEA,³⁾ and that the photoproducts of 1, 2, 4-TCB in acetonitrile were 1, 4-DCB (major), 1, 3-DCB, and

1, 2-DCB (major) and 1, 3-DCB with 1, 2, 3-TCB in decreasing sequence.

Fig. 5 shows the photodechlorination pathways and photoproducts of TCBS in a TEA

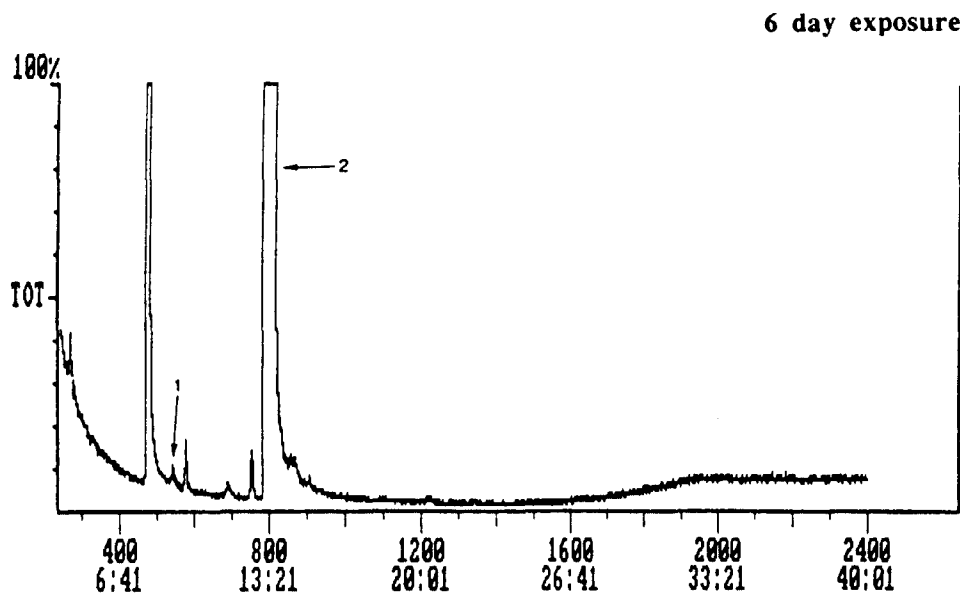


Fig. 6. Total ion chromatogram of 1, 2, 3-TCB in TEA solution after 6-day exposure (Experiment 2).

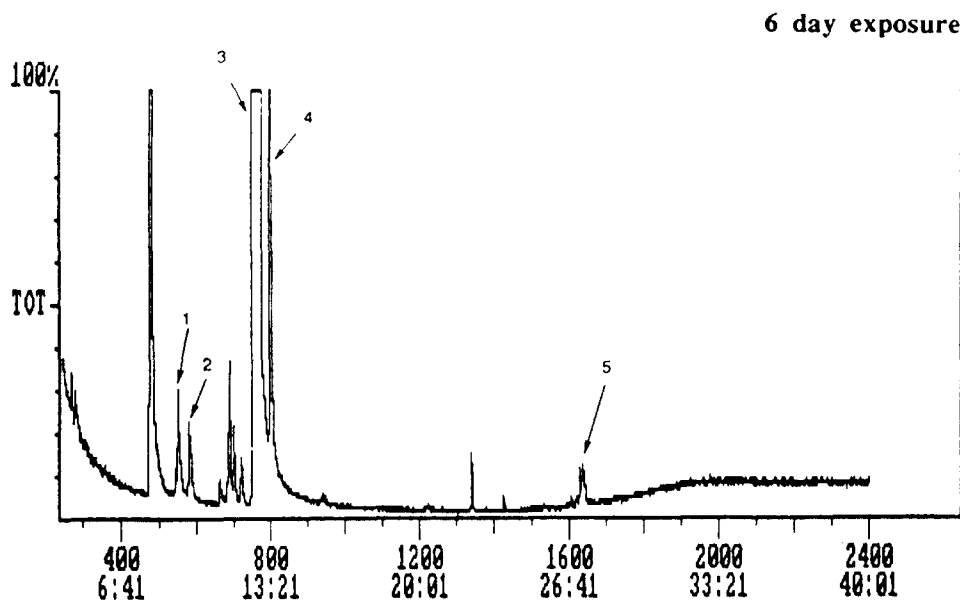


Fig. 7. Total ion chromatogram of 1, 2, 4-TCB in TEA solution after 6-day exposure (Experiment 2).

solution.

Total ion chromatograms (Experiment 2) of 1, 2, 3- and 1, 2, 4-TCB in TEA solutions are shown in Fig. 6 and 7.

3. Comparison of TCB Photoproducts between Nitrite Solution and TEA Solution

It was found that the photoreaction of TCBs in nitrite solution proceeds through nitration of TCBs to subsequently yield their corresponding trichlorophenols, dichlorophenols and PCBs. It was observed that more dechlorinated photoproducts were produced in Experiment 1. Of particular interest with respect to the difference in reactivity among the isomers is the observation that 1, 2, 4-TCB is much more reactive to nitrite than 1, 2, 3- or 1, 3, 5-TCB, as shown from the chromatograms. The formation of PCB was evident when 1, 2, 4-TCB was irradiated under black lamp in nitrite solution forming five different PCB congeners which are formed by dichlorobenzene radicals and TCBs by a coupling reaction. Whereas, a small peak of PCB was detected from 1, 2, 4-TCB in TEA solution in both Experiment 1 and 2. No PCB was detected in nitrite solution using the sun lamp. Compared to the TEA sensitizer, nitrite gave higher yields of PCBs (pentachlorinated PCBs) when 1, 2, 4-TCB was irradiated under black lamps. Although 1, 3, 5-TCB in TEA solution was not dechlorinated under the black lamp irradiation, it produced 1, 3-dichlorobenzene under the sun lamp, reflecting that experimental conditions of Experiment 1 induced more reactivity than those of Experiment 2.

CONCLUSION

The present work suggests that TCBs when photolyzed with nitrite are converted to TCNBs through nitration and that the parent compounds undergo dechlorination and subse-

quently hydroxylation to TCPs. Different experimental conditions produced a variety of photoproducts, mostly dechlorinated products. However TCPs via the nitro-nitrite mechanism did not occur. The major photoproducts by TEA sensitization were dichlorobenzenes. But TEA was proven not to be enough to dehalogenate TCBs in aqueous solution. These preliminary findings will provide a better understanding of the fate of TCBs or provide mechanisms for the removal processes of TCBs in the environment.

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