Photodegradation of Polychloronaphthalenes in Methanol Solution

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Introduction

Polychlorinated naphthalenes (PCN, Halowaxes) are industrial compounds with properties and uses similar to the polychlorobiphenyls (PCB), in addition the former compounds have been identified in commercial PCB preparations (STALLING and HUCKINS, 1973; DeVOS et al, 1970).

It has been suggested the PCN might interfere in organochlorine insecticide analysis in a manner analogous to that of the chlorobiphenyls (AMOUR and BURKE, 1971). Furthermore, PCN have been implicated in causing various diseases, such as chloracne, liver damage and chick edema (KIMBROUGH, 1972).

Since PCN are potential environmental pollutants it is of interest to determine their photochemical breakdown patterns and the nature of the products obtained in order to evaluate their toxicity and permanence in the ecosystem. Among the individual isomers chosen for this study some of the major components present in Halowax mixtures can be found. Both monochlorinated naphthalenes have been observed in Halowaxes 1031, 1000, 1001, and 1099, as well as the 1,2- and 2,3-dichloronaphthalenes and the 1,3,5,8- and 1,2,3,4-tetrachloronaphthalenes (BELAND and GEER, 1973).

Chloronaphthalenes exhibit moderate absorption in the 300 nm region due to a π-π^* transition. As in other haloaromatics, interaction of the lone pair electrons of the halogen with the π system leads to an excited state with some C-X antibonding character (MAJER and SIMMONS, 1964) so that bond fission might be expected. At 300 nm the incident energy is sufficient to cause C-Cl bond fission.

Methods and Materials

The dichloronaphthalenes were all synthesized by unambiguous methods from the corresponding diamines or chloroamines. The tri- and tetrachloro naphthalenes were kindly supplied by the Imperial Chemical Industries and their generosity is gratefully appreciated. The purity of the samples was checked by glc (>99%). Methanol used in photolyses (BAKER) was of spectrophotometric grade and was distilled before use. All other solvents were analytical grade (BAKER) and were used without further purification. Benzophenone (ALDRICH) was twice recrystallized from ethanol.

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Irradiation Procedures. All photolyses were carried out in the presence of atomospheric amounts of oxygen using a Rayonet Photochemical Reactor (The Southern N.E. Ultraviolet Co.) fitted with RUL3000 lamps having apeak energy output at 300 nm.

During irradiation the samples (4 ml) were contained in Pyrex tubes (uv cutoff~ 285 nm) fitted with Teflon stoppers. The chamber temperature was approximately 30°. A merry-go-round apparatus was employed to insure equal exposure of all samples to uv radiation.

Sunlight irradiations were carried out on solid films in quartz vessels.

Analytical Procedures. Gas chromatography was carried out on Hewlett-Packard model 5710A apparatus equipped with a 6' x 1/8" i.d. glass column packed with 3% SE-30 on 80-100 mesh Chromosorb W. This column was operated isothermally in the 120-180° range or with programming from 120-280° (4°/min).

Detection of products was by flame ionization, with injector and detector temperatures at 300°.

To separate 1- and 2-chloronaphthalene a 25% 1,2,3-(triscyanoethoxy) propane on Gas Chrom Q, 20' x 1/16" i.d. copper column was operated isothermally at 90°. Both columns were operated with a helium carrier gas flow of 30 ml/min.

For product identification, retention times and mass spectra were compared with those of authentic samples where available. Mass spectrometry was carried out using a Varian Associates Model 1700 gas chromatograph interfaced directly with a Varian MAT Model CH7 mass spectrometer operated at 70 eV ionizing voltage.

Only the dechlorination products were quantitated; no standards were available for quantitation of the dimers formed, their number sometimes exceeding thirty different compounds.

Results and Discussion

In methanol solution dechlorination and dimerization were the major reaction pathways. Small amounts (<2%) of methoxylated naphthalenes were also detected. Several methoxylated dimers were also observed. Formation of binaphthyl derivatives appears to result from arylation rather than radical coupling. The major products may most easily be accommodated by a free radical mechanism. Simple chloronaphthalenes photolyze in this manner (RUZO, BUNCE and SAFE,1974), as do other haloaromatic compounds (KHARASCH and SHARMA, 1968). Cleavage of the aryl chloride affords an aryl radical which may abstract hydrogen from the solvent or attack a molecule of starting material or product to form binaphthyls.

Degassed solutions with benzophenone concentrations (0.15 M) such that PCN can only react by energy transfer, show the same

Table 1. Photoproducts and Relative Reaction Rates of Polychloronaphthalenes in Methanol Solution

Substituent[a]	% Dechlorination	Relative Rate[c]
1,8-Cl_2	86[b]	56.0
1,2-Cl_2	25[b]	10.1
1,3,5,8-Cl_4	80	9.0
1-Cl	28[b]	8.6
2,7-Cl_2	6	8.3
2,3-Cl_2	25	8.0
1,4-Cl_2	10	6.3
2-Cl	15	5.9
1,2,3-Cl_3	25[b]	5.1
1,3,7-Cl_3	4	5.1
1,3,6-Cl_3	7	4.9
2,3,6-Cl_3	5	4.4
1,4,6,7-Cl_4	4	4.0
1,3,5-Cl_3	6	4.0
1,5-Cl_2	2	4.0
1,2,6-Cl_3	36	3.4
1,3,5,7-Cl_4	1	2.3
1,2,3,5-Cl_4	20	2.4
1,4,6-Cl_3	11	2.0
1,2,3,4-Cl_4	80	1.0

[a] 120 hr irradiations, 1-5x10^{-3}M solutions

[b] 40 hr irradiations

[c] the absolute rates are of the order of 10^{-9}M sec^{-1}.

rate of reaction as that of unsensitized samples. This fact, coupled with observations showing that oxygen quenches the reaction to about a third of its degassed rate, lends support to the intermediacy of a triplet excited state.

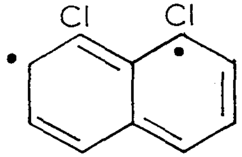
The small amounts of methoxylated products observed probably arise through nucleophilic displacement of halogen by the solvent, such as has been previously reported (BARLTROP et al, 1967) for other haloaromatic systems.

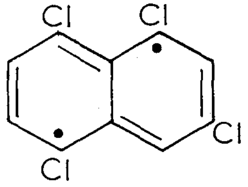
With the exception of 1,2-dichloronaphthalene, which gave an approximately equal mixture of 1- and 2-chloronaphthalene, all other dichlorinated isomers gave as the only dechlorination product the corresponding monochloronaphthalene. Most tri- and tetrasubstituted naphthalenes gave mixtures of dechlorination products. A few, however, gave a single peak in the glc. 1,3,5,8-Tetrachloronaphthalene yield a trichloronaphthalene whose glc retention time was identical with that of the 1,4,6 isomer (m/e 230). 1,3,5,7-Tetrachloronaphthalene gave a product with the retention time of 1,3,7-trichloronaphthalene.

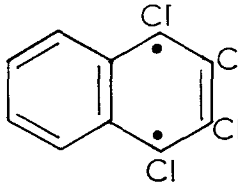
In all cases the major binaphthyl obtained was that arising from attack of an initially formed radical on a molecule of starting material. For the dichloronaphthalenes the major dimer had M^+ at m/e 356, for the trichloronaphthalenes at m/e 424 and for the tetrasubstituted PCN at m/e 492. The isomeric monochloronaphthalenes gave chlorobinaphthyls (m/e 288) as the major components of the dimer mixture.

The wide range of the dechlorination/binaphthyl ratio indicates marked substituent effects; in general, those PCN with vicinal or *peri* substitution afford larger amounts of dechlorinated products, while unhindered PCN give mostly dimers. Thus, 1,8-dichloronaphthalene shows an unusually high proportion of dechlorination product and a large relative reaction rate (about nine times that of the 1,4-isomer). Correspondingly 1,3,5,8-tetrachloronaphthalene is more reactive than its 1,2,3,4-analog by a similar factor. In addition, the 1,8-isomer is one of the few PCN for which stabilization of the triplet diradical over both chlorines is not possible. The increased possibility for resonance stabilization of the triplet biradical in the higher chlorinated compounds may be the reason for their slower reactions. Additionally, *peri* interactions between the chlorines in the 1 and 8 positions might be responsible for the enhanced reactivity.

It may be that both electronic and steric factors influence the rates and products observed. This situation is analogous to that of the tetrachlorobiphenyls where electronic and steric factors have a marked effect on the magnitude of their reaction ratio (RUZO, ZABIK and SCHUETZ, 1974).







Thus, on the basis of stabilization through delocalization of the diradical pair in the proximity of halogen atoms, it is not surprising to find that the higher chlorinated PCN react slower than those containing fewer chlorines, as opposed to observations in other aromatic systems where a larger number of halogen atoms increases the reaction rate because of enhanced absorption in the UV.

It has recently been reported (GULAN et. al, 1974) that the higher chlorinated components of Halowaxes showed faster degradation rates. These apparently contradictory results can be explained on the basis of the difference in the extinction coefficients (ε) between the PCN of high and low chlorine content. In Halowaxes the former will absorb most of the incident radiation due to their larger ε values in the >300 nm region, thus the light absorbed by the lower chlorinated PCN will not be sufficient to cause appreciable degradation. It is also possible that since the latter have higher triplet energies (E_T) they will act as sensitizers for the degradation of the heavier isomers.

Sunlight irradiations of Halowax 1014, 1,5-dichloronaphthalene and 2-chloronaphthalene as solid films of quartz gave only insoluble polymeric material. Since the solution photochemistry data clearly indicate facile generation of radicals it is not surprising that the solid state photolyses yield polymeric products. 2,3-Dichloronaphthalene irradiated by sunlight in methanol solution yielded the same products as in 300 nm photolysis.

These results show the possibility of environmental degradation through photochemical pathways, which may prove more efficient than metabolic routes for the chloroaromatics.

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