Beiträge zur Ökologischen Chemie LXXIII[1] Irradiation Studies of Aldrin and Chlordene Adsorbed on a Silica Gel Surface

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The conversion of several cyclodiene pesticides during UV-irradiation has been previously reported. In particular, the photochemical reactions of aldrin and chlordene have been investigated in solution (ROSEN and CAREY, 1966; BENSON et al., 1971; VOLLNER et al., 1971), in solid phase as a thin film on glass (ROSEN and SUTHERLAND, 1967; BENSON et al., 1971) and in gas phase (PARLAR and KORTE, 1972). However, these are not the only types of reactions that can occur at the environmental level. For example very little is known about the behaviour of the chlorinated cyclodiene pesticides which have been adsorbed on the surface of particulate matter.

In a model study we have investigated the UV-conversion of aldrin and chlordene adsorbed on a silica gel surface and compared them with the solid phase reactions where the compounds were deposited on a glass surface.

MATERIALS AND METHOD

Materials: Flutec PP 1 i.e. perfluoro-n-hexane, C_6F_{14}, b.p. 53° C (Kali-Chemie AG, Hannover), n-hexane, acetone, benzene, chloroform and carbon tetrachloride (E. Merck, Darmstadt). The same silica gel was used for UV-adsorption studies and column separations (Kieselgel 60, 70 - 230 mesh ASTM and with a specific surface area of 450 sq. m/g, E. Merck, Darmstadt).

Apparatus and Instruments: The irradiation apparatus comprised a cylindrical metal drum (diameter: 30 cm, volume: 4, 5 l) with a quartz tube (diameter: 7 cm, length: 25 cm) inserted along its axis. The pyrex (or quartz) cooling finger and the mercury high pressure lamp (HPK 125 W Philips, with wavelengths above 230 nm) were placed axially within the open-ended quartz tube. While the drum and the quartz tube were rotated axially (belt driven at 20 rpm) the silica gel was internally tumbled and mixed by means of regularly spaced metal fins attached to the inside wall of the drum.

A conventional soxhlet apparatus was used for the adsorption of aldrin and chlordene onto the silica gel surface. The soxhlet thimble was pre-extracted with Flutec PP 1 prior to use.

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[1] For part LXXII see NITZ et al. (1974)

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Structural confirmation was obtained using a LKB 9000 S GC-MS combination and a Perkin-Elmer 90 MHz NMR spectrometer.

PROCEDURES AND RESULTS

a) Adsorption on Silica Gel: To 600 ml of Flutec in a 1 l r.b. flask was added 120 g silica gel. 0, 5 g of gaschromatographically pure aldrin (or chlordene) was placed in the soxhlet thimble and the whole extracted for 30 hours.

b) Pyrex Irradiation: Of the 120 g silica gel containing the adsorbed pesticide only 100 g was used for irradiation purposes. The remaining 20 g was found to have adsorbed 54, 6 mg aldrin (and 65, 2 mg in the case of chlordene). During the irradiation small aliquots were periodically removed to monitor the conversion process. The final work up of the remaining silica gel, 73, 0 g in the case of aldrin and 66, 5 g for chlordene, included exhaustive extraction with acetone. Thus it could be calculated that a total of 199, 3 mg aldrin (and 216, 8 mg chlordene) were used for column chromatography after irradiation with long wavelength UV-light (pyrex, $\lambda \geq$ 290 nm) for 16 hours (and 23 hours for chlordene).

c) Column Chromatography: 30 g silica gel was placed in a column (diameter: 3 cm, length: 30 cm) which was successively eluted with n-hexane, carbon tetrachloride and chloroform after application of the aldrin extract. In the case of chlordene the solvents used were n-hexane and benzene. Table 1 gives the unchanged and reacted amounts of the parent pesticides. The yields of the respective products obtained from reacted aldrin and chlordene are shown in Table 2.

d) Quartz Irradiation: The above irradiation experiments were repeated using a quartz cooling finger ($\lambda \geq$ 230 nm). Comparable results were obtained to those found with pyrex but with shorter irradiation times. Aldrin required only 1 hour for approximately 50 % conversion of starting material, while chlordene required

Table 1

	Aldrin		Chlordene	
Quantity irradiated	199, 3 mg	(100, 0 %)	216, 8 mg	(100, 0 %)
Quantity unchanged	32, 5 mg	(16, 3 %)	115, 5 mg	(53, 3 %)
Quantity reacted	166, 8 mg	(83, 7 %)	101, 3 mg	(46, 7 %)

1, 5 hours. Again the main products were the epoxides (51, 8 % dieldrin and 40, 3 % chlordene epoxide were found). However, with quartz the amounts of polymer and polar products were larger than found in the pyrex experiments. Of particular interest was the isolation of heptachlor in 5, 1 % yield from quartz but not pyrex irradiation.

DISCUSSION

In the case of UV-conversion in the solid phase as a thin film on a glass surface the major products have been shown to be the respective cross linked photo-isomers with only minor amounts of epoxide (ROSEN and SUTHERLAND, 1967; BENSON et al., 1971).

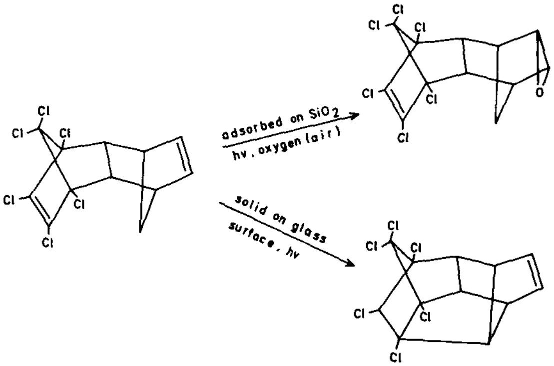

Figure 1

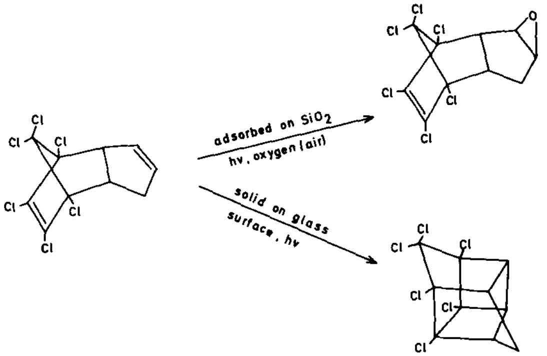

Figure 2

Therefore it was anticipated that the products of conversion on an adsorbed surface would be similar to those obtained in the solid phase with possibly minor differences in yield. However, as seen from Table 2, the major products were the respective epoxides of aldrin and chlordene together with only minor amounts of the photoisomerisation products (Figures 1 and 2).

Thus it can be postulated that the differences between the products from the solid and adsorbed phases are due to the extent of contact between the parent pesticides and oxygen. In the solid phase on a glass surface it is only the pesticide molecules at the pesticide/air interface that can form the respective epoxides and other oxidation products (see Table 2), the underlying pesticide molecules being photochemically converted to other products. In the adsorbed phase however, a monomolecular layer probably exists and because of the greater dispersion of pesticides there is more pesticide/air contact resulting in far higher yields of epoxide.

There are some reactive species of oxygen such as $O(^3P)$, O_3, $O_2(^3\Sigma_g^-)$, $O_2(^1\Delta_g)$. It has been shown that $O(^3P)$ and O_3 can lead to epoxidation of reactive double bonds (CVETANOVIC, 1963; MURRAY, 1968; CRIEGEE, 1973). However, it can be estimated that the wavelength used in the above pyrex experiments ($\lambda \geq$ 290 nm) cannot form these two species in sufficient amounts to explain such high yields of epoxides. In photooxidation reactions involving ground state $O_2(^3\Sigma_g^-)$ and singlet oxygen $O_2(^1\Delta_g)$, no epoxide end products have been reported to our knowledge (GOLLNICK, 1968; KEARNS, 1971). Thus the mechanism by which aldrin and chlordene are photooxidised on a silica gel surface to their respective epoxides cannot be described without doubt at present.

It is obvious that the photoisomerisation reactions which are the main reactions in solid, solution and gas phase occur as side reactions with very small yields in the adsorbed phase. This implies that an intramolecular mechanism is replaced by an intermolecular mechanism. These results should thus be considered in the discussion of the conversion of cyclodiene pesticides. From the above experiments it can be concluded that low levels of cyclodiene pesticides such as aldrin and chlordene (with a reactive double bond) adsorbed on airborne particulate matter may degrade via their epoxides and other oxidation products rather than their UV-photoisomerisation products.

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Table 2

	Quantity (mg)	Conversion (%)		Quantity (mg)	Conversion (%)
Aldrin reacted	166, 8	100, 0	Chlordene reacted	101, 3	100, 0
Products[+]			Products[+]		
Dieldrin[++]	110, 1	63, 9	Chlordene epoxide[++]	59, 8	56, 4
Photoaldrin	8, 5	5, 1	Photochlordene	3, 4	3, 4
Photodieldrin	4, 6	2, 7	1-*exo*-Hydroxychlordene	16, 7	15, 7
Photoketoaldrin[+++]	8, 1	4, 7	Ketochlordene	7, 9	7, 5
			Unidentified product ($M^+ = 350\ Cl_6$)	7, 8	7, 4
Polymer and polar products (not chromatographable)	-	23, 6	Polymer and polar products (not chromatographable)	-	9, 6

[+] All identifications were done by TLC, GLC, MS, NMR and melting point comparisons with authentic standards.

[++] Both epoxides have the *exo*-epoxide configuration.

[+++] Ketone II as described by BIENIEK and KORTE (1969) .

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