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Dicofol Solubility and Hydrolysis in Water

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Dicofol [1,1-bis(4'-chlorophenyl)2,2,2-trichloroethanol, Kelthane] is a miticidal pesticide that is a less toxic analogue of DDT. Dicofol has been used commercially since the early 1950's, and a patent (U.S. 2,812,362) describing its preparation was issued in 1957. Dicofol is inert to oxidation (MARCH 1958) and has been found to be persistent in soils over a five year period (HARRIS and MILES 1975). The half life of dicofol on and in the rind of oranges and lemons has been determined to be greater than 200 and 125 days, respectively (GUNTHER et al. 1957). These facts suggest that natural microbes in agronomic ecosystems do not readily metabolize this pesticide.

Under other conditions, dicofol degrades to 4,4'-dichlorobenzophenone (DBP). JOHNSON (1976) has observed that DBP is produced from dicofol in anaerobic sewage sludge. Furthermore, the thermal conversion of dicofol to DBP is a very common pathway included in the proposed environmental degradation of DDT (KENAGA 1972). Dicofol also decomposes to DBP in the presence of alkali (BERGMANN and KALUSZYNER 1958, MELKNIKOV 1971), but since it is nearly insoluble in water, the decomposition to DBP is generally observed in non-aqueous (ethanol-ammonia) solutions. In fact, the rapid conversion of dicofol to DBP in ethanol-ammonia solutions is the basis for a routine spectrophotometric determination of this compound (GUNTHER and BLINN 1957). Dicofol on almond hulls partially converts to DBP during washing with regular tap water and oven drying (ARCHER 1969). The removal of dicofol, and conversion to DBP, from the almond hulls was much faster and quantitative when the wash water was mildly alkaline.

Although there have been few measurements of dicofol or DBP in aquatic ecosystems, one could hypothesize from available data that the persistence of dicofol in water would depend mostly on its solubility and its rate of conversion to DBP at natural pH levels. The objective of this report is to experimentally

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assess this hypothesis.

EXPERIMENTAL

Most chromatographic analyses were performed on a gas chromatograph utilizing a flame ionization detector. The column used was a 180 cm x 2 mm (I.D.) stainless steel tube packed with commercial 3% SP-2100 (methyl silicone) on 80/100 mesh Supelcoport. Low resolution mass spectra were obtained either by GC/MS or by direct probe introduction. Liquid chromatographic separations were performed on a Waters liquid chromatograph equipped with a Model 660 solvent programmer, two Model 6000 pumps, and a Model 440 dual absorbance detector. A C_{18}-μ-Bondapak column (30 cm x 3.9 mm I.D., 10μ particle size) was used with a methanol/water gradient (30-100% MeOH in 20 min at a total flow rate of 2 ml/min).

Purified dicofol (96%) was obtained from Rohm and Haas. LC and GC/MS analyses of this standard detected trace quantities (<1% of dicofol) of 4,4'-dichlorobenzil, 1,1-bis(4'-chlorophenyl)2,2-dichloroethylene, 1,1-bis(4'-chlorophenyl)1,2,2,2-tetrachloroethane, and 4,4'-dichlorobenzophenone. Further purification was not considered necessary.

The aqueous solubility of dicofol was determined following a standard procedure (SMITH et al. 1977). The solid dicofol was equilibrated in 1 liter of distilled water, pH 6-7, with gentle stirring over a period of seven days at 20-23° C. At the specified time interval, the dicofol/water mixture was filtered through either a 0.45 μm pore Millipore filter or a glass fiber Whatman filter (effective pore size of 1 μm). The aqueous filtrate was then extracted with dichloromethane (1:10 organic to water volume ratio), evaporated, and analyzed by GC. These experiments were done in duplicate.

The transformation to dicofol in aqueous media was investigated by adding either a 210 μg aliquot of dicofol in 50 μL of methanol or about 20 mg of the solid to 500 mL of water at a specific pH and then mixing gently with a Teflon stirring bar. After a definite time interval, any organic transformation processess were quenched by extracting the solution with 50 mL of dichloromethane. The organic extract was evaporated to dryness, reconstituted to 100 μL with cold (0° C) dichloromethane, and analyzed by GC/MS and HPLC. Standards were similarly prepared. An inert

internal standard, 2(2'-hydroxy-3',5'-di-t-butylphenyl)-5-chloro-2H-benzotriazole, was added to all systems to monitor extraction efficiency and to enhance analytical accuracy.

Since some other workers have observed that DBP can be produced from dicofol by pyrolysis during gas chromatographic analyses (ZWEIG and SHERMA 1972), we took extra precautions to insure that our experiments did not exhibit this artifact. For example, repeated GC and GC/MS analyses of a dicofol standard solution (2 μg/μL) showed no spurious production of DBP. In addition, many GC analyses were repeated using HPLC; consistant results were obtained in all cases. We attribute our successful results to the use of a glass-lined injection port operating at modest temperatures (270° C).

RESULTS AND DISCUSSION

The solubility of dicofol in distilled water at 20° C, as determined by filtration of the saturated solution through a glass fiber filter (1 μm effective pore size), was measured to be 0.8 μg/mL. Filtration through a 0.45 μm pore size Millipore filter gave a solubility of 0.3 μg/mL. Solubility differences due to the effective filtration pore size for physical occlusion were probably negligible for the two types of filters. The lower dicofol solubility measured by filtration with the Millipore filter may, however, be due to chemical absorption of soluble dicofol. The adsorption of dicofol on the glass fiber filter was determined to be less than twenty percent by GC analyses of filtered and unfiltered aliquots of the same sample of dicofol solubilized in water.

In the determination of dicofol water solubility, no dichlorobenzophenone was detected in the filtrates. The conversion of dicofol to dichlorobenzophenone was observed, however, (and confirmed by HPLC and GC/MS analyses) when dicofol in methanol was added to aqueous solutions as described earlier. Extensive GC, GC/MS, and HPLC analyses showed that no other products were being formed. The percent conversions to DBP under varying conditions are summarized in Table 1. The conversion is proportional to pH, substantiating the previously mentioned alkaline hydrolysis hypothesis. At pH's of 10.2 and 8.2, hydrolysis was complete in 24 h. Further hydrolysis tests at these pH values over shorter time intervals indicated that the conversion approximated first order kinetics, and give half-lives of 3 ± 1 min and 60 ± 5 min for the pH values of 10.2 and 8.2, respectively.

An aliquot of a 2 h dicofol alkaline (8.2) hydrolysis solution was filtered through a 1 μm glass fiber filter and analyzed by extraction and GC, along with an unfiltered aliquot. These analyses revealed that the DBP present in the unfiltered aliquot was not in the filtered aliquot, indicating that the DBP is either insoluble or is efficiently adsorbed by the glass fiber filter. Thus, DBP may have been formed during the solubility equilibration experiments but did not pass through the filter. The aqueous solubility of 0.8 μg/mL for dicofol must, therefore, be considered a minimum value.

TABLE 1

Conversion of Soluble Dicofol[a] to DBP in Various Aqueous Solutions

pH	Time (h)	Percent Conversion to DBP	Percent Dicofol Recovery	Aqueous Medium
1	24	0	88	H_2O/HCl
1	24	35	75	H_2O/HCl
1	72	0	82	H_2O/HCl
2	24	0	86	H_2O/HCl
2	72	0	84	H_2O/HCl
3	24	0	87	H_2O/HCl
3	72	0	91	H_2O/HCl
5	24	32	92	KH_2PO_4/OH
5	24	34	99	KH_2PO_4/OH
7	0.5	25	99	KH_2PO_4/OH
7	1	19	97	KH_2PO_4/OH
7	24	38	95	KH_2PO_4/OH
7	24	58	88	KH_2PO_4/OH
7	1	100	95	pH 7 Commercial
8.2	24	100	99	$NaHCO_3$
8.2	24	100	94	$NaHCO_3$
10.2	24	100	90	Na_2CO_3
10.2	24	100	94	Na_2CO_3

[a]Dicofol concentration, 0.4 μg/mL, added in methanol; T=20-23° C.

At the pH values of 5 and 7, hydrolysis tests for time intervals between 1 and 48 h were not repro-

ducible in terms of percent conversion of dicofol to DBP, and did not appear to follow first order kinetics. For example, at pH 7, the percent conversion of dicofol to DBP was <25 percent over a one hour interval, but was about 50 percent over a 24 h interval. In addition, when the hydrolysis was carried out in a commercial pH 7 buffer which contained methylbenzethonium chloride [Merck Index No. 5897] (added as a mold inhibitor but also acting as a surfactant), the conversion to DBP was complete within one hour. Except for one anomalous case, there was no conversion of dicofol to DBP under acidic conditions over time periods ranging up to 72 h. Since dicofol is synthesized under acidic conditions, these results are to be expected.

The hydrolysis of solid phase dicofol gave significantly different results. A 250 µg aliquot in dichloromethane was placed on the walls of the flask, and the solvent was evaporated. One half liter of aqueous media at a specific pH was then added to the flask. After a time interval of gentle stirring, the solution was extracted as previously described. The results of these studies are presented in Table 2. These data indicate that conversion of solid phase dicofol to DBP is considerably slower than when it is added to the aqueous solution in a miscible solvent (methanol). Solid dicofol was also added to pH 8.2 and 10.2 solutions to make saturated mixtures. After 24 h, the entire mixture was extracted (without filtration) and analyzed by GC. The conversion of dicofol to DBP was <1% in all cases. A logical explanation for these observations is that the hydrolysis of dicofol is limited by its rate of solubilization, which is probably dependent upon particle size and may also be affected by pH, ionic strength, and matrix constituents.

TABLE 2

Conversion of Solid Dicofol to DBP at pH 8.2

Time (h)	Percent Conversion to DBP	Percent Dicofol Recovery
1	0	83
3	0	75
10	38	98
16	88	97
24	100	94

The hydrolysis of dicofol in Charles River water (pH = 7.5) was also studied. Dicofol in methanol was added to both filtered (1 μm pore glass fiber) and non-filtered river water which was then stirred for 24 h and extracted as described previously. The results are presented in Table 3. The most intriguing result in this experiment is the poor recovery for both filtered and unfiltered samples. Both biological organisms and the presence of natural organic constituents may effect recovery by either degrading dicofol or by inhibiting its extraction. It is apparent from Table 3 that the conversion of dicofol to DBP, for the amounts recovered, is greater for the filtered water samples. This may indicate that in the unfiltered samples, some of the soluble dicofol adsorbs onto suspended particulates and hydrolyzes slower, if at all. Based on an n-octanol/water partition coefficient of 10^5, estimated from the data of LEO et al. (1971), the major fraction of soluble dicofol in a natural water system at equilibrium should be adsorbed onto suspended particles or sediments. Adsorption, however, must kinetically compete with hydrolysis and possible biodegradation. The data in Table 3 indicate that all three processes are active, at least in Charles River water.

TABLE 3

Conversion of Soluble Dicofol to DBP in Charles River Water; pH 7.5; Duration of Experiment 24 h

River Water	Percent Conversion to DBP	Percent Dicofol Recovery
Filtered	94	60
Filtered	88	28
Unfiltered	58	36
Unfiltered	47	43

The solubilization and hydrolysis of solid dicofol in river water was also considered. Solid dicofol was added to make a saturated mixture that was stirred gently for 24 h. The entire mixture was extracted, without filtration, and analyzed by GC. The percent conversion to DBP was <1% for two separate samples.

While there is little doubt that soluble dicofol hydrolyzes to DBP at moderate pH values (8-10) and in

relatively short times, it is not at all certain to what degree this may occur in natural waters. As has been shown, the physical phase in which dicofol is introduced into water has a significant effect on its eventual fate; the hydrolysis of soluble dicofol has to compete with physical adsorption and possible biological degradation. It is, therefore, of greater benefit to study hydrolysis in natural waters rather than in laboratory solutions. In Charles River water, soluble dicofol was observed to hydrolyze in a relatively short time. Due to variations in suspended loads, pH, organic matter, and other matrix constituents, the rate of hydrolysis of any soluble dicofol in other river waters may be significantly different, and should be assessed on an individual basis.

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