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The Hydrolysis Rate of Diamidafos in Dilute Aqueous Solution

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INTRODUCTION

Because of the great importance of assessing the potential contribution by pesticides to environmental contamination, a study was carried out to determine the fate of diamidafos (proposed common name) N,N'-dimethyl-phenylphosphorodiamidate (the active ingredient of NELLITE® nematicide[a]), in water. The efficacy of this compound has been well demonstrated (YOUNGSON 1959, YOUNGSON and GORING 1963, TURNER 1963). The study reported herein defines the hydrolysis rates at different pH and temperature values, gives the observed activation energy for the reaction, and describes the products.

MATERIALS AND METHODS

Chemicals - N,N'-Dimethyl-$^{14}C_2$-phenylphosophorodiamidate, diamidafos-^{14}C, was prepared using a procedure described by MEIKLE (1968). This compound as used was 96.9% radiochemically pure; specific activity, 1.186 mCi/mmole.

N-Methyl-^{14}C-hydrogenphenylphosphoroamidate and dihydrogenphenyl phosphoric acid were prepared as described by MEIKLE and CHRISTIE (1969).

[a] A registered trademark of the Dow Chemical Company, Midland, Michigan.

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Methods - Hydrolysis reactions were carried out using 10 ml of solution in 20-ml screw cap bottles with Teflon liners. pH was maintained with 0.05M buffer solutions: acetate at 4.1, phosphate at 7.1, and borate at 7.9.

The hydrolysis reactions were conducted in cabinets which served the dual purpose of maintaining a constant temperature ($\pm$0.2°C) and of providing a dark environment to avoid confounding photolysis reactions.

The concentration of diamidafos at the start of the hydrolysis reaction was 7.82×10^{-5} molar; the material was 96.9% radiochemically pure.

Analysis of radioactive diamidafos hydrolysis samples was carried out using paper chromatography (PC) as follows: Ten-µl aliquots were withdrawn and applied to Whatman No. 3 paper (1 inch wide). The paper strips were developed descending at ambient temperature with benzene saturated with water. In all cases, known compounds were run on the same paper strips. This solvent system gave the R_f ranges for compounds involved shown in Table I. Other solvent systems are also shown.

Paper chromatograms were examined for radioactivity by incremental counting. One-cm segments were placed in scintillation vials and treated with methanol, 1 ml per counting vial, to desorb radioactive compounds; this mixture was assayed for radioactivity in a toluene-based cocktail. The chromatography counting data were analyzed using a computer program which enabled us to describe the distribution of significant radioactive areas on the chromatograms, at the 95% level of confidence, as a percent of the total radioactivity on the paper strip.

TABLE I

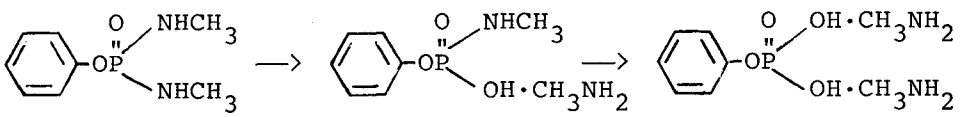
PAPER CHROMATOGRAPHY OF DIAMIDAFOS AND ITS POTENTIAL HYDROLYSIS PRODUCTS

Compound	R_f ranges in solvent system...[a]			
	I	II	III	IV
Diamidafos	0.85-0.97	0.80-0.94	0.25-0.46	0.90-0.96
N-Methylhydrogenphenyl phosphoroamidate	0.52-0.60	0.66-0.76	0	0.17-0.27
Dihydrogenphenyl phosphate	0-0.06	0.18-0.29	0	
N,N'-Dimethylhydrogen phosphorodiamidate	0.63-0.69	0.70-0.78	0	
N-Methyldihydrogen phosphoroamidate	0.47-0.53	0.23-0.58	0	

[a] Solvent system I was n-butanol saturated with water; II was ethanol/15N ammonia/water (10/1/4, v/v); III was benzene saturated with water; and IV was n-butanol/benzene/water (1/9/10, v/v).

It was discovered that methyl-^{14}C-amine, present as a product in the hydrolysis mixture, was retained by the paper chromatogram in solvent system I. After developing and drying the chromatogram, this compound was still present at the origin, held there as a salt of the hydrolysis products of diamidafos-^{14}C. The methyl-^{14}C-amine was removed by exposure of the appropriate paper segment to nonradioactive methylamine vapors in a closed container. The source of methylamine was a 40% aqueous solution. The paper segments were exposed for 1 week, and the methylamine was changed five times during this period. Longer exposure did not remove any additional radioactivity, thus indicating that the radioactive methylamine was effectively exchanged by this treatment.

Radioactive assay of the appropriate paper segments, before and after removal of methyl-^{14}C-amine, enabled us to calculate the concentration of dihydrogenphenyl phosphoric acid, one of the hydrolysis products of diamidafos-^{14}C, in spite of the fact that the compound was not radioactive. The following development demonstrates how this was done. This reaction was the one being followed



with the radioactive label in the methylamine portion of the molecule. The following is a schematic representation in this reaction:

$$A\text{-}{}^{14}C_2 \longrightarrow B\text{-}{}^{14}C + M\text{-}{}^{14}C \longrightarrow C + 2M\text{-}{}^{14}C.$$

The percent of total radioactivity and counts on a paper strip contributed by each radioactive area was known from an assay of the paper strip. One-half of the counts for

diamidafos-^{14}C on the developed paper chromatogram represented the concentration of A remaining (because A has two radioactive carbons). The counts at the origin, after removal of methyl-^{14}C-amine, represented the concentration of B (remember that C was not radioactive and could not contribute to the counts at the origin). The difference between origin counts before and after removal of methyl-^{14}C-amine represented the concentration of methyl-^{14}C-amine (M) formed in the hydrolysis reaction. The concentration of C, then, was defined as (M-B)/2. The proportions of A, B and C in the reaction mixture were calculated as follows: A/(A+B+C), etc. These were then converted to molar concentration values.

RESULTS AND DISCUSSION

Table II shows the micromolar concentration, as a function of time and temperature, for diamidafos-^{14}C and its hydrolysis products in 0.05M acetate buffer, pH 4.1; Tables III and IV show the data for the reaction in 0.05M phosphate buffer, pH 7.1, and in 0.05M borate buffer, pH 7.9, respectively.

Linear regressions of ln concentration on days for each temperature and acetate buffer, pH 4.1 (Table II) are shown in Table V. No measurable hydrolysis of diamidafos-^{14}C occurred in the phosphate buffer, pH 7.1 (Table III) nor in the borate buffer, pH 7.9 (Table IV).

The observed activation energy E_{ob} for diamidafos-^{14}C hydrolysis, calculated from the rate constants in Table V using the equation, $\ln k_{ob} = \ln A_{ob} - E_{ob}/RT$, is 5.3 Kcal/mole, standard error 0.4. A_{ob} is a constant known as the frequency factor, T is the absolute temperature, and R is the gas constant taking the value 1.986 cal./deg./mole.

TABLE II

HYDROLYSIS OF DIAMIDAFOS-^{14}C IN 0.05M ACETATE BUFFER, pH 4.1

Time, days	Molar concentration x 10^6 of ...[a]								
	Diamidafos at...			B at ...			C[b] at...		
	15°	25°	38°	15°	25°	38°	15°	25°	38°
0	78.3	78.3	78.3	2.6	2.6	2.6	-0.1	-0.1	-0.1
1	77.7	76.8	76.2	3.5	3.5	3.6	-0.5	0.5	1.0
2	77.0	73.5	72.1	2.9	4.9	5.8	0.8	2.4	2.9
5	74.5	71.8	65.4	4.9	6.0	11.1	1.4	3.0	4.2
9	68.5	65.0	56.8	7.8	8.4	7.7	4.4	7.4	16.3
15		58.3	53.7		11.9	17.8		10.4	9.3
22	60.4	53.7	45.3	15.7	14.4	16.2	4.6	12.7	19.3

[a] B is N-methyl-^{14}C-hydrogenphenylphosphoroamidate and C is dihydrogenphenyl phosphoric acid. Temperature is °C.

[b] The negative values arise because they are calculated values, and they suggest the variability in the method.

TABLE III

HYDROLYSIS OF DIAMIDAFOS-^{14}C IN 0.05M PHOSPHATE BUFFER, pH 7.1

Time, days	Molar concentration x 10^6 of ...[a]					
	Diamidafos at...		B at ...		C[b] at ...	
	15°	38°	15°	38°	15°	38°
0	78.2	78.2	3.0	3.0	-0.5	-0.5
1	78.1	79.3	2.6	2.2	0	-0.8
2	78.5	77.8	2.4	4.4	-0.2	-1.5
5		78.4		2.6		-0.2
9	78.5	78.2	2.5	3.0	-0.2	-0.5
15	78.2	78.3	2.3	2.3	0.3	0.1
22	78.0	77.4	2.2	3.4	0.5	0

[a] B is N-methyl-^{14}C-hydrogenphenylphosphoroamidate and C is dihydrogenphenyl phosphoric acid. Temperature is °C.

[b] The negative values arise because they are calculated values, and they suggest the variability in the method.

TABLE IV

HYDROLYSIS OF DIAMIDAFOS-^{14}C IN 0.05M BORATE BUFFER, pH 7.9

Time, days	Molar concentration x 10^6 of ...[a]					
	Diamidafos at...		B at ...		C[b] at ...	
	15°	38°	15°	38°	15°	38°
0	78.3	78.3	2.9	2.9	-0.4	-0.4
1	78.4	79.0	2.2	2.4	0.2	-0.6
2	78.3	76.0	2.2	4.1	0.2	0.6
5	78.4	77.7	2.5	2.9	-0.2	0.1
9	78.5	76.8	2.3	3.5	0	0.4
15	78.4	76.8	2.3	3.5	0	0.4
22	77.4		2.7		0.7	

[a] B is N-methyl-^{14}C hydrogenphenylphosphoroamidate and C is dihydrogenphenyl phosphoric acid. Temperature is °C.

[b] The negative values arise because they are calculated values, and they suggest the variability in the method.

TABLE V

LINEAR REGRESSION OF Ln CONCENTRATION ON DAYS FOR HYDROLYSIS OF DIAMIDAFOS-^{14}C IN ACETATE BUFFER pH 4.1[a]

Temperature, °C	K_{ob}, day^{-1}	SE of[b] K_{ob}	Half-life, days	Calc'd. initial concn. $M \times 10^6$	Correlation coefficient
15	0.0122	0.0008	56.8	78.4	0.992
25	0.0174	0.0009	39.8	77.4	0.993
38	0.024	0.002	28.4	75.9	0.983

[a] The regression equation has the form: $\ln C = \ln C_o - k_{ob} t$, where C_o is the initial concentration of diamidafos-^{14}C and k_{ob} is the observed rate constant (t^{-1}).

[b] SE is the standard error.

As pointed out by MEIKLE, et. al (1973), the magnitude of E_{ob} can be a useful indicator of the nature of a reaction when a compound such as diamidafos is studied for its mode of decomposition in biological environments such as soil and natural waters. The low activation energy for the hydrolysis of diamidafos in acetate buffer, pH 4.1, suggests that catalysis is operating. This appears to be a case of acid catalysis, but no distinction can be made between specific oxonium-ion catalysis and a general acid catalysis because the necessary changes in acetate buffer concentration were not studied for their effect on the hydrolysis rate (HAMMETT 1940).

At pH 7.1 and 7.9, no detectable chemical hydrolysis of diamidafos took place within a period of 22 days. At pH 4.1, the chemical hydrolysis rate, enhanced by an apparent acid catalysis, was such that at 25°C the half-life was 39.8 days (Table V).

Acid hydrolysis of diamidafos yielded N-methyl-hydrogen phosphoroamidate and dihydrogenphenyl phosphate. The phosphoroamidate was identified by PC where the radioactive compound was exactly coincident with authentic compound in the four solvent systems listed in Table I. Since the two potential radioactive hydrolysis products in which the phenyl group is not present (Table I) were not detected by paper chromatography, the excess exchangeable methyl-^{14}C-amine always appearing at the origin in the benzene/water solvent system (Table I) indicated the presence of dihydrogenphenyl phosphate, even though this compound was not radioactive and, thus, could not be detected directly. Additionally, it is not likely that this phenyl phosphate will decompose further because, with few exceptions, the dianions of monoalkyl and monoaryl phosphates are unreactive under the conditions of this reaction (BENKOVIC 1972).

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