The implications of these findings are that the cheeky yam (*D. bulbifera* var *rotunda*) is not toxic, but due to its diosbulbin content, it is bitter. This is in contrast to the toxic alkaloid-containing yam (*D. hispida*), which did not contain any of the bitter components detected by our tests. Traditional Australian processing techniques effectively remove the bitter compound. Further research on the distribution of bitter varieties of *Dioscorea* may be useful not only for chemotaxonomy but also for ethnabotanical studies.

ACKNOWLEDGMENT

We thank the aboriginal people of Donydji and Gapuwijak for collecting specimens of cheeky yam and Dr. N. G. White, Genetics Department, La Trobe University, and R. Yilarama and R. Walker, Gapuwijak Resource Centre for assistance in Arnhem Land. Specimens of *D. hispida* were obtained from Thailand, courtesy of Benjavon Carumapattana, Forest Products Research Division, Royal Forestry Department, Bangkok, and Dr. Phichai Tovivich, South-East Asian Network for the Chemistry of Natural Products, which also supported B.T.'s visit to Thailand.

Registry No. Diosbulbin D, 66756-57-8; dioscorine, 3329-91-7.

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Received for review March 8, 1984. Accepted June 7, 1984. W.B. was supported by a postgraduate fellowship from the Australian Institute of Aboriginal Studies. We gratefully acknowledge the help and support provided by the South-East Asian Network for Natural Products of Chemistry, both in collecting the material and by other means.

High-Performance Liquid Chromatographic Determination and Hydrolysis Studies of Phenyl Phosphorodiamidate, a Urease Inhibitor

Ernest R. Austin,* Timothy J. Bradford, and Michael S. Lupin[1]

A high-performance liquid chromatographic (HPLC) method was developed for the determination of phenyl phosphorodiamidate (PPDA). This method was employed in a kinetic study of the hydrolysis of PPDA in the pH range of 2–12 at temperatures of 25, 35, and 45 °C. Two parallel competing reactions were observed: The acid-catalyzed reaction produced ammonia and phenyl phosphoramidate; the base-catalyzed reaction yielded phenol and phosphorodiamidic acid. Phenol and phenyl phosphoramidate were also determined by HPLC. Apparent first-order rate constants were determined for the hydrolysis of PPDA as a function of pH and temperature. Activation energies of 9.4 and 18.0 kcal/mol were obtained for the acid- and base-catalyzed reactions, respectively.

Improving the efficiency of urea as a source of fertilizer nitrogen in the developing countries is a major objective of the International Fertilizer Development Center (IFDC). One aspect of this work that has received much attention recently is the addition of a urease inhibitor, such as phenyl phosphorodiamidate (PPDA), to urea applied to flooded rice to reduce the rate of urea hydrolysis and subsequent ammonia volatilization loss. Extensive field trials are presently being conducted in Asia and elsewhere. As part of the support program for the agronomic research currently being conducted, a high-performance liquid chromatographic method has been developed both to determine PPDA and to study its hydrolysis.

Urea hydrolysis to ammonia and carbon dioxide is catalyzed by the enzyme urease present in the soil. It has been shown (Vlek and Craswell, 1979) that rapid hydrolysis of urea applied to flooded rice can cause ammonia volatilization losses of up to 50% of the applied nitrogen. Vlek and Craswell (1981) discussed the factors influencing ammonia volatilization from flooded systems and possible approaches for preventing such losses. One such approach is the use of an additive that would inhibit the urease-catalyzed hydrolysis of urea. Heber et al. (1979) described the use of PPDA as a urease inhibitor for upland crops

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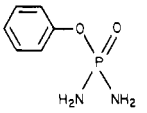
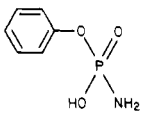
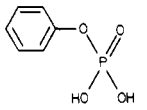
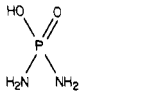
Table I. Reference List of Chemicals and Abbreviations

abbreviation	chemical name	structure
PPDA	phenyl phosphorodiamidate	
PPA	phenyl phosphoramidate	
PPP	phenyl phosphate	
PDAA	phosphorodiamidic acid	

such as ryegrass and oats. Byrnes et al. (1983) showed that PPDA is effective in delaying urea hydrolysis, maintaining a lower pH in the floodwater, reducing ammonia concentrations, and decreasing ammonia volatilization losses. However, they found that the effectiveness of PPDA was limited to about 11 days. It was necessary therefore to examine the stability of PPDA in order to understand the limitation of the effectiveness of PPDA as a urease inhibitor.

Indirect spectrophotometric methods have been used for determining PPDA (Wenzel et al., 1981). Spectrophotometry has also been used to study the base hydrolysis of substituted phenyl phosphorodiamidates (Williams and Douglas, 1972) and the hydrolysis of ethyl phosphorodiamidate in the pH range of 2–10 (Woelke et al., 1977). The object of this work was to develop a fast, accurate, analytical procedure for low concentrations of PPDA and to study its hydrolysis as a function of pH and temperature with the HPLC method developed.

MATERIALS AND METHODS

Chemicals. PPDA was obtained from ICN Pharmaceuticals, Plainview, NY, and was used as received after being checked by HPLC for purity. Phenyl disodium phosphate was obtained from Fisher Scientific. A reference list of chemicals, along with abbreviations and structures, is given in Table I.

Apparatus. The chromatographic system used was a Perkin-Elmer Series 2 high-performance liquid chromatograph (HPLC) equipped with a Rheodyne 7125 injection valve, a Water's RCM 100 radial compression module, and a Perkin-Elmer LC-55 UV–visible spectrophotometer. Chromatograms were recorded on a Leeds and Northrup Speedomax recorder and integrated by a Columbia Scientific programmable computing integrator. A 10-μL sample was injected by using the filled-loop method. Separation was accomplished using a Water's C-18, 5-μm radial cartridge. The mobile phase was a mixture of methanol and a 1% KH_2PO_4 solution, which flowed at 1.5 mL/min. The percentage of methanol in the mobile phase was 30% for studying the acid hydrolysis of PPDA and 50% for studying the basic hydrolysis. The detector was operated at a wavelength of 200 nm.

Calibration of HPLC. The HPLC was calibrated for PPDA, phenol, and phenyl phosphoramidate (PPA) by preparing a series of standard solutions of each compound and injecting them into the HPLC. For PPDA a stock solution (20.9 mg/100 mL) was prepared, and a series of five standards was made by diluting 1, 2, 3, 4, and 5 mL of stock solution to 25 mL. Each solution was injected 3 times, and an average area was calculated for each standard. These average values were plotted with their corresponding concentrations. A linear least-squares line was determined and plotted with the data. The linearity of the data was checked visually, and the correlation coefficient was calculated. A sensitivity factor was obtained from the slope of the least-squares line.

Table II. Calibration Data for PPDA, Phenol, and PPA

compd	sensitivity, μmol L^{-1} μV^{-1} s^{-1}	correlation coeff	% methanol in mobile phase
PPDA	6.86×10^{-3}	0.9999	20
phenol	9.24×10^{-3}	0.9999	30
PPA	6.70×10^{-3}	0.9999	30

In a similar manner a stock solution of phenol (49.0 mg/250 mL) was prepared. Two standards were made by diluting 5 mL of stock solution to 50 mL and 10 mL of stock solution to 25 mL. These two solutions along with the stock solution were analyzed by HPLC, and calibration data were obtained as described for PPDA.

A stock PPA solution was prepared by weighing 200 mg of the monosilver salt of PPA, adding it to $\cong$200 mL of distilled water, treating it with an excess of HCl, filtering it to remove AgCl, and diluting it to 500 mL. Two standards were prepared by diluting 10 and 20 mL of this stock solution to 100 mL. These two standards were then analyzed by HPLC, and calibration data were obtained as described for PPDA. The calibration data for PPDA, phenol, and PPA are summarized in Table II.

Buffers. In the pH range of 2–8, a 1% solution of KH_2PO_4 was adjusted to the desired pH value with H_3PO_4 or KOH solution. The pH 9 and 10 solutions were prepared from a 1% solution of K_2HPO_4 adjusted in a similar manner. The pH 11 and 12 solutions were made from a 1% solution of $Na_3PO_4 \cdot 12H_2O$ that was adjusted with H_3PO_4 solution to the desired value. Because the pH 9 solution did not hold a constant pH during the experiment, a pH 9 solution was made from a 5% solution of $Na_3PO_4 \cdot 12H_2O$ by adjusting it with H_3PO_4 solution.

Method. Typically 99 g of the desired buffer solution was weighed into a glass vessel and placed in a constant-temperature bath. After temperature equilibration, 1 mL of PPDA solution (approximately 4 mg/mL) was added to the container to initiate the reaction and the timer was started. The reaction solution was agitated continuously, sampled periodically with a syringe, and analyzed by HPLC.

A sample chromatogram is shown in Figure 1. This is a chromatogram of a PPDA hydrolysis experiment at pH 5.5 and 45 °C after 1454 min of reaction time. The mobile phase was 30% methanol in aqueous phosphate buffer solution and flowed at 1.5 mL/min. Retention times for PPA, PPDA, and phenol were 2.40, 3.87, and 7.88 minutes, respectively. The chromatographic conditions were chosen so that the PPA peak would be resolved from the negative water peak while keeping the total analysis time to a minimum. These conditions were used for experiments at pH 6.5 and below where PPA was observed as a product. Above pH 6.5 the percentage of methanol in the mobile phase was increased to 50%. This decreased the retention times of PPDA and phenol to 2.88 and 4.61, respectively, and thus reduced the total analysis time.

At pH 2, 11, and 12 the reaction was too rapid for routine sampling so a quenching technique was employed. In this case only 98 g of buffer solution was weighed into the reaction vessel. The reaction was initiated by adding 1 mL of PPDA solution and then quenched after the desired reaction time by adding 1 mL of KOH or H_3PO_4 solution

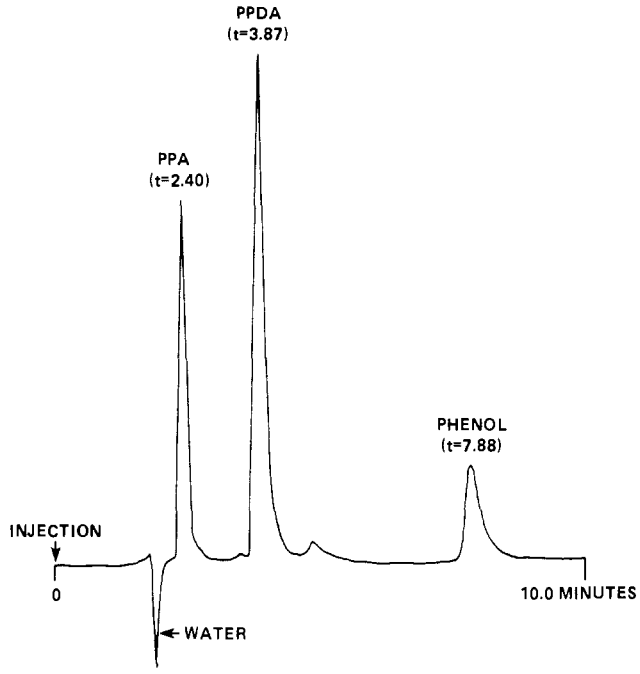


Figure 1. Chromatogram of a PPDA hydrolysis experiment (pH 5.5 and 45 °C) after 1454 min of reaction time. The concentrations of PPA, PPDA, and phenol were 9.5, 23.6, and 4.2 μg/mL, respectively. Retention times in minutes are given on the chromatogram. The mobile phase was 30% methanol and 70% buffer solution flowing at a rate of 1.5 mL/min.

Table III. Comparison of the Elemental Analyses of the Silver Salts Formed from the Acidic and Basic Decomposition Products of PPDA with $C_6H_7NO_3PAg$ and $H_4N_2O_2PAg$, Respectively

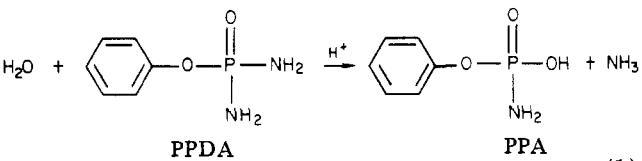
element	$C_6H_7NO_3$ PAg	silver salt from acid hydrolysis[a]	$H_4N_2O_2$ PAg	silver salt from basic hydrolysis
carbon	25.74	25.64		
hydrogen	2.52	2.54	1.99	1.99
nitrogen	5.00	4.88	13.81	13.50
phosphorus	11.06	11.01	15.27	15.47
silver	38.53	38.38	53.17	52.98

[a] This salt was obtained by hydrolyzing PPDA under acidic conditions in the presence of silver ions from $AgNO_3$. When silver ions were not present during hydrolysis but added only after the conversion to PPA was expected to be complete, the silver salt obtained was a mixture of the monosilver salt of PPA and the disilver salt of PPP.

as required to attain a pH between 5 and 7. After quenching, a sample of the solution was analyzed by HPLC.

RESULTS AND DISCUSSION

Hydrolysis Mechanisms. Two hydrolysis pathways have been identified. In acid conditions, cleavage of one P–N bond occurs with the liberation of ammonia and the formation of PPA (eq 1). The composition of PPA was



(1)

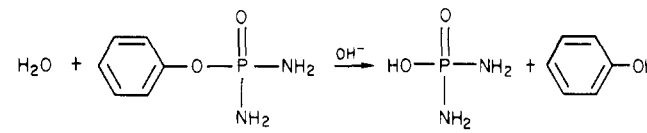
confirmed by isolating it as its monosilver salt, which was characterized by complete elemental analysis (Table III). Acidification of the silver salt and reinjection into the HPLC column confirmed its retention time. Ammonia was not detected by HPLC under the conditions employed in this study; however, the liberation of ammonia was confirmed by steam distillation and titration of the ammonia.

Additional study of the acid hydrolysis of PPDA at pH 2 showed that PPA is not a stable product. By use of a mobile phase containing only 5% methanol in aqueous phosphate buffer flowing at 1.5 mL/min, resolution of the phenyl phosphate (PPP) and PPA was obtained. The retention times were 5.00 and 5.49 min for PPP and PPA, respectively. Under these conditions PPDA had a retention time of 20.2 min. HPLC analysis of sequential samples from the pH 2 hydrolysis showed that PPDA was essentially totally decomposed in ≅20 min. At this point, the concentration of PPA reached its maximum and then slowly decreased. A new peak appeared in the chromatograms shortly after the reaction was initiated. The concentration of this compound increased slowly with time as the PPA slowly decreased. The new compound was PPP. This identification was based on comparable retention times for the new peak and phenyl disodium phosphate, ammonia analysis that indicated greater than 1 mol of ammonia produced/mol of PPDA, and elemental analysis of a silver salt obtained from acid hydrolysis of PPDA that indicated the salt was a mixture of the monosilver salt of PPAA and the disilver salt of PPP.

Although PPA is not stable under acidic conditions, it is more stable than PPDA. At pH 2 PPDA disappeared in ≅20 min, whereas PPA was still at 74% of its maximum obtained value after 138 min of reaction time. These results are in agreement with those obtained for the hydrolysis of ethyl phosphorodiamidate under acid conditions (Woelke et al., 1977).

Under the chromatographic conditions used in the remainder of this study, i.e., a mobile phase containing 30–50% methanol, PPA and PPP would be eluted simultaneously. However, little PPP would be produced in the reaction times studied since PPA is much more stable than PPDA. In addition, the numerical kinetic results presented in this study were based solely on the disappearance of PPDA and not on the formation of products.

In basic conditions, cleavage of the P–O bond occurs with the liberation of phenol and the formation of phosphorodiamidic acid (PDAA) (eq 2). PDAA was not detected by HPLC under the conditions employed in this study; however, its production was confirmed by isolation of its monosilver salt, which was characterized by complete elemental analysis (Table III). Phenol was identified by its retention time on the HPLC column. Liberation of phenol occurs at pH as low as 5.5 at 45 °C.



(2)

Kinetics. The hydrolysis of PPDA at constant pH was found to be a first-order process in the pH range of 2–12 at temperatures of 25, 35, and 45 °C. This is expressed in integral form in eq 3 where [PPDA] is the concentration

$$[\text{PPDA}] = [\text{PPDA}]_0 \exp(-k_{\text{PPDA}}t) \quad (3)$$

of PPDA at time t, $[\text{PPDA}]_0$ is the initial concentration of PPDA, and k_{PPDA} is the pseudo first-order rate constant for the loss of PPDA. This equation can be linearized by putting it into logarithmic form as shown in eq 4. Since

$$\ln([\text{PPDA}]/[\text{PPDA}]_0) = -k_{\text{PPDA}}t \quad (4)$$

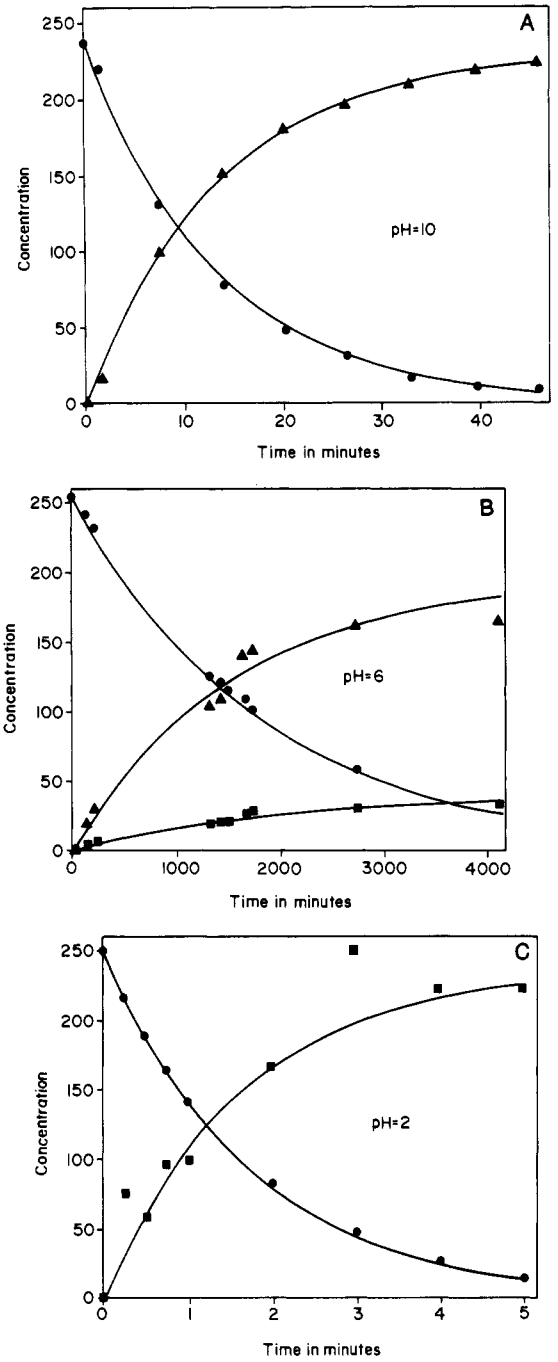


Figure 2. Experimentally determined concentrations (micromole per liter) of PPDA (●), phenol (▲), and PPA (■) at 45 °C and three different pH values as a function of reaction time. The solid lines are calculated from eq 3, 7a, and 7b.

the chromatographic peak height or area is proportional to the concentration of PPDA, eq 4 may be rewritten in terms of PPDA peak area or height. Equation 5 shows

$$\ln [\text{PPDA area}/(\text{PPDA area})_0] = -k_{\text{PPDA}}t \quad (5)$$

this, using PPDA area. Values for PPDA rate constants were obtained by applying the method of linear least squares to the data in the form of eq 5. The values obtained are given in Table IV. It should be noted that many of the kinetic runs were repeated with urea present in the reaction mixture at a high concentration (4 mg/mL) relative to the PPDA concentration (0.04 mg/mL). The presence of urea produced no significant change in the values of the rate constants.

Some typical data depicting three different pH regions are given in Figure 2. At pH 10, phenol is the only hydrolysis product detected by HPLC. At pH 2, PPA is the only product detected by HPLC. At pH 6, both phenol and PPA are detected simultaneously. The symbols represent the actual data points, and the lines are calculated from the theoretical expressions given in 3, 7a, and 7b.

Table IV. Experimentally Determined Apparent First-Order Rate Constants (k_{PPDA}) for the Hydrolysis of PPDA in the pH Range of 2–12 at 25, 35, and 45 °C

pH	k_{PPDA}, min^{-1}		
	25 °C	35 °C	45 °C
2.0	2.14×10^{-1}	3.54×10^{-1}	5.78×10^{-1}
3.0	2.14×10^{-2}	3.54×10^{-2}	5.85×10^{-2}
4.0	2.11×10^{-3}	3.24×10^{-3}	6.05×10^{-3}
5.0	2.30×10^{-4}	4.65×10^{-4}	8.79×10^{-4}
5.5	7.71×10^{-5}	1.74×10^{-4}	4.10×10^{-4}
6.0	5.19×10^{-5}	1.65×10^{-4}	5.50×10^{-4}
6.5	7.52×10^{-5}	3.57×10^{-4}	1.07×10^{-4}
7.0	1.32×10^{-4}	6.76×10^{-4}	2.17×10^{-3}
7.5	1.86×10^{-4}	1.12×10^{-3}	3.40×10^{-3}
8.0	2.65×10^{-4}	1.57×10^{-3}	3.24×10^{-3}
9.0	3.31×10^{-3}	9.73×10^{-3}	3.02×10^{-2}
10.0	9.79×10^{-3}	3.01×10^{-2}	7.57×10^{-2}
11.0	9.76×10^{-2}	2.59×10^{-1}	6.42×10^{-1}
12.0	8.94×10^{-1}	2.28	4.56

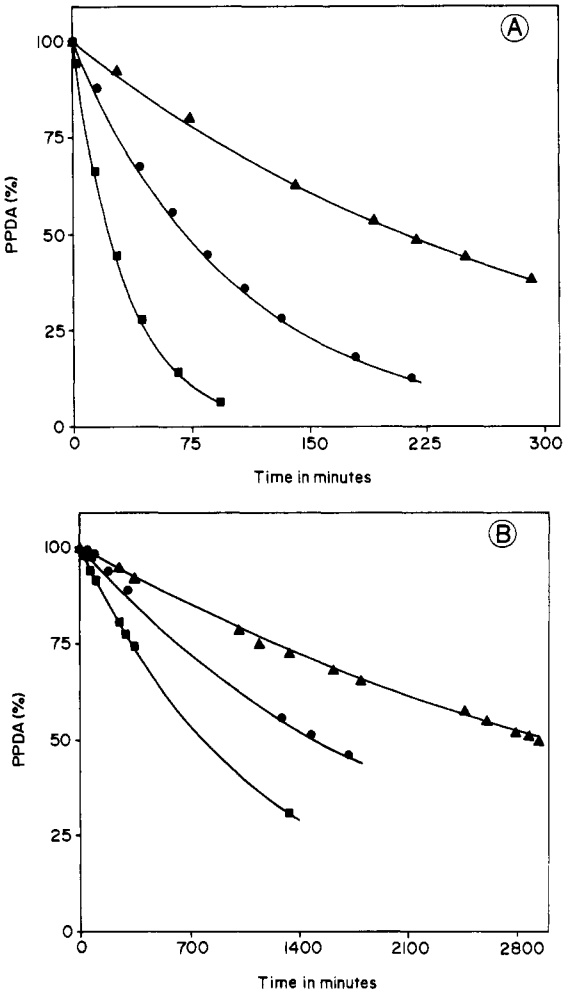


Figure 3. Effect of temperature on the hydrolysis of PPDA in the basic region (A) at pH 9 and in the acidic region (B) at pH 5. The temperatures are 25 (▲), 35 (●), and 45 °C (■).

Parts A and B of Figure 3 show the effect of temperature on the hydrolysis rate of PPDA at pH 9 and 5, respectively. Although both the acidic and basic hydrolysis rates increase with increasing temperature, the basic hydrolysis rate is affected more than the acidic rate.

Figure 4A,B shows the effect of pH on the hydrolysis

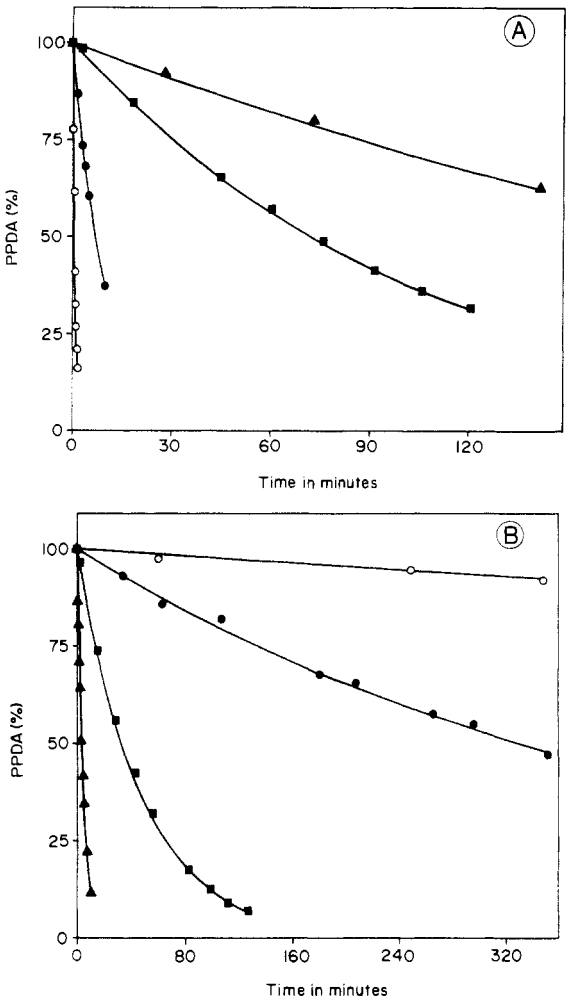


Figure 4. Effect of pH on the hydrolysis of PPDA at a constant temperature of 25 °C. In the basic region (A) data are shown at pH 9 (▲), pH 10 (■), pH 11 (●), and pH 12 (○). In the acidic region (B) data are shown at pH 2 (▲), pH 3 (■), pH 4 (●), and pH 5 (○).

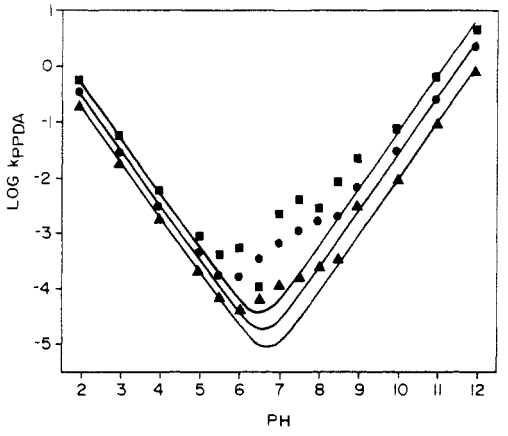


Figure 5. Log of the apparent first-order rate constant for the loss of PPDA as a function of pH at 25 (▲), 35 (●), and 45 °C (■). The solid curves are calculated by using eq 9.

rate at a constant temperature of 25 °C. The hydrolysis rate increases in the extreme acidic and basic regions in essentially a linear fashion with increasing hydronium and hydroxyl ion concentration. However, at comparable concentrations of these two ions the basic reaction is more rapid than is the acidic reaction. For example, at 25 °C the rate constant at pH 12 is approximately 5 times greater than the rate constant at pH 2.

Table V. Values for Acidic and Basic Rate Constants Used in Equation 9

temp, °C	k_A, L mol^{-1} min^{-1}	k_B, L mol^{-1} min^{-1}
25	21.4	95.0
35	35.4	263
45	58.2	618

The decomposition of PPDA proceeds by two competing parallel reactions.

$$\text{PPDA} \xrightarrow{+H^+,\ k_A} \text{PPA} + NH_3 \quad (6a)$$

$$\text{PPDA} \xrightarrow{+OH^-,\ k_B} \text{Phenol} + \text{PDAA} \quad (6b)$$

In the extreme acidic region only PPA is detected, and in the extreme basic region only phenol is detected. In the intermediate pH region the two reactions compete, and the amounts of phenol and PPA produced depend on the pH and the values of k_A and k_B.

The formation of products from the first-order hydrolysis of PPDA can be expressed as given in eq 7a and 7b where k_A is the rate constant for the production of PPA

$$[\text{PPA}] = [\text{PPDA}]_0\left(\frac{k_A}{k_A + k_B}\right)[1 - \exp[-(k_A + k_B)t]] \quad (7a)$$

$$[\text{phenol}] = [\text{PPDA}]_0\left(\frac{k_B}{k_A + k_B}\right)[1 - \exp[-(k_A + k_B)t]] \quad (7b)$$

and k_B is that for the production of phenol. PPA and phenol concentrations were obtained from their respective chromatographic peak areas or heights by multiplying by the appropriate sensitivity factors.

On this basis, the overall rate constant for the hydrolysis can be expressed as given in eq 8.

$$k_{PPDA} = k_A[H^+] + k_B[OH^-] \quad (8)$$

This can be written in terms of pH as given in eq 9.

$$k_{PPDA} = 10^{-pH}k_A + 10^{(pH-14)}k_B \quad (9)$$

Figure 5 shows a comparison of the values predicted by eq 9 with the experimentally determined rate constants. Here the logarithm of the rate constants is plotted as a function of pH values for the three experimental temperatures. In general, there is good agreement between the experimental values and the mathematical expression in the pH ranges of 2–5 and 10–12. At the lower temperatures these ranges are extended to 2.0–5.5 and 8.5–12.0. The reason for the large deviation in the middle pH region has not been determined. However, this is the region where both hydronium and hydroxyl ions are at a low concentration simultaneously. In this region the measured rate constant values are greater than the values predicted by eq 9. This may indicate that the kinetic model is incomplete and that some additional factor is enhancing the decomposition of PPDA in this pH region. Possibly the phosphate buffer contributes to this enhancement.

The rate data obtained in the middle pH region are important when considering PPDA as an additive to urea fertilizer since this pH region is typical of soil pH values. However, in flooded soil systems chemical decomposition is only one mode by which PPDA would be destroyed. Microorganisms and surface sorption reactions may also degrade PPDA. The relative importance of these modes of degradation should be determined.

The values for k_A and k_B were obtaind from eq 9 by using the data from Table IV in the extremely acidic and

basic regions. The pH 2 and 3 data produced values for k_A, and the pH 10, 11, and 12 data produced values for k_B. The averages of these values are given in Table V. Applying the Arrhenius rate constant theory to the values obtained for k_A and k_B yields an activation energy of 9.4 kcal/mol for the acid hydrolysis and 18 kcal/mol for the base hydrolysis of PPDA. Although these activation energies indicate that the acid hydrolysis would be faster than the base hydrolysis, the Arrhenius A factor for the base hydrolysis is 5×10^6 times greater than the A factor for the acid hydrolysis and thus overshadows the difference in the activation energies.

Registry No. PPDA, 7450-69-3; PPA, 45951-59-5; PDAA, 10043-91-1; NH_3, 7664-41-7; phenol, 108-95-2; urease, 9002-13-5.

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Received for review March 19, 1984. Accepted June 4, 1984.

Starch Matrix for Controlled Release of Urea Fertilizer

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Methods are described for blending urea and a nitrogen stabilizer with starch and converting the blend to particles for potential application as a controlled-release nitrogen source for agriculture. Depending upon the technique used, 5-g samples of the particles released 15–40% and 15–60% of the formulated urea when exposed to 30 and 50 mL of water for 1 h, respectively. Nitrapyrin was slowly volatilized from moist particles, but evaporation from dry particles was negligible.

Some fertilizers, especially urea, are so water soluble that they are readily leached from the crop root zone or cause plant damage due to excessive concentrations. Approaches to obviate these disadvantages have included the development of synthetic fertilizers such as urea–formaldehyde and the use of protective coatings of sulfur (Dalal and Prasad, 1975), bitumens (Elbe et al., 1979), or coal tar (Reddy and Prasad, 1975).

While controlled-release systems are showing considerable success, there are instances where coatings may crack during shipment and also where the release of nutrients is too slow for certain applications. This paper describes two methods for blending urea with starch to yield granular products having potential for application where fast rates of release are desirable. One method utilizes the recently reported technique for encapsulating a wide variety of pesticides (Shasha et al., 1984). An aqueous, alkaline dispersion of starch or flour and urea is rendered particulate by blending with boric acid and then with dry starch. The second method involves extruding a gelatinized dispersion of starch, urea, and water followed by either pelletizing or grinding to the desired particle size. Either method allows the inclusion of other chemicals such as nitrogen stabilizers or sulfur, often used to improve the efficiency of nitrogen fertilization.

EXPERIMENTAL SECTION

Commercially available corn starch, 10.5% moisture (CPC International, Englewood Cliffs, NJ), and pregelatinized corn flour, 4% moisture (Illinois Cereal Mills, Inc., Paris, IL) were used. Nitrapyrin [N-serve, 93% active 2-chloro-6-(trichloromethyl)pyridine, technical grade] was obtained from Dow Chemical Co., Midland, MI. All other chemicals, including urea, were reagent grade.

Extrusion Method (Table I). Urea and, optionally, KOH were first dissolved in water (45 mL of H_2O/55 g of total formulation solids) and then blended with air-dried starch for 45 min at 95–100 °C in a Brabender mixer (type R.E.E.-6, manufactured by C. W. Brabender Instruments, Inc.). The mixture was then extruded with an extrusion head attached to a Brabender Plasti-Corder Type PL-V300 at a barrel temperature of 105 °C. The screw of the extruder was 1.9-cm diameter; it had a length:diameter ratio of 12 and a compression ratio of 2:1. The die had four holes of 1.5-mm diameter each. After drying at ambient conditions, the extrudate strands were reduced to particles passing 8 mesh by grinding with a Waring Blendor. Two products listed in Table I (no. 82 and 83) were extruded through a 1 mm diameter die and cut to 2–3 mm lengths with scissors prior to complete drying to simulate pelletizing.

Starch and Flour Borate Method (Table I). In a Waring Blendor at 25–30 °C, pregelatinized corn flour was dispersed in a solution of urea, water (50 mL of H_2O/50 g of urea), and concentrated ammonium hydroxide (4 mL/100 g of final dry product). Then boric acid (2 g/100 g of final product) was mixed with the gelatinized flour–urea mixture to form a rubbery product. Air-dried corn starch (18 g/100 g of final product) was then added slowly with stirring, which caused the rubbery mass to break down into particles passing 8 mesh. On a dry basis these formulations contained 2% boric acid, 18% ungelatinized starch, and 80% urea and gelatinized flour. The percentage starch or flour reported in Table I for this method

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