Kinetic Study of the Decomposition of Methyl [1-(Butylcarbamoyl)-1*H*-benzimidazol-2-yl]carbamate (Benomyl) to Methyl 1*H*-Benzimidazol-2-ylcarbamate (MBC)

Raj P. Singh[‡] and Ian D. Brindle

Chemistry Department, Brock University, St. Catharines, Ontario L2S 3A1 Canada

C. David Hall

Ontario Ministry of the Environment, 125 Resources Road, Rexdale, Ontario M9W 5L1, Canada

Mikio Chiba*

Research Station, Agriculture Canada, Vineland Station, Ontario L0R 2E0, Canada

The kinetic study of the degradation of benomyl to methyl 1*H*-benzimidazol-2-ylcarbamate (MBC) in pure water and in aqueous solutions at pH 1–7 has been carried out by using reversed-phase high-performance liquid chromatography (RP-HPLC) at room temperature (21 ± 1 °C). The values of first-order rate constants (k) for the degradation reaction were similar (k = 2.5–3.7 × 10^{-5} s^{-1}) in the pH range 2–7, but at high acid concentration (pH 1.0) the rate constant showed a sharp decrease (k = 1.0 × 10^{-5} s^{-1}). This may be due to the protonation of benomyl at low pH where a sharp increase in its solubility was also observed. Quantitative conversion of benomyl to MBC was not observed in acetonitrile; instead, due to the reversible nature of the reaction, at equilibrium about 12% benomyl remained intact. The rate constants for the forward reactions in acetonitrile were found to be 2.5 × 10^{-4} s^{-1} at 21 ± 1 °C and 3.3 × 10^{-4} s^{-1} at 25 ± 1 °C. In mixed solutions of water with buffer, acetonitrile, or methanol the degradation of benomyl slowed down with the increase in water concentration.

INTRODUCTION

The fungicide benomyl [methyl [1-(butylcarbamoyl)-1*H*-benzimidazol-2-yl]carbamate] is one of the most widely used systemic fungicides (Delp, 1987), but its movement in the environment is still not clearly understood. One of the major reasons for this is because it is difficult to trace the behavior of benomyl in water, owing to its low solubility. Another reason was that, as suggested in the early days after its introduction, once dissolved in water, it rapidly decomposes to MBC (methyl 1*H*-benzimidazol-2-ylcarbamate) (Clemons and Sisler, 1969; Peterson and Edgington, 1970), which is also fungicidal.

Later studies proved that it is possible to dissolve a large quantity of benomyl in organic solvents and that its rate of decomposition in these solvents is very fast (Chiba and Doornbos, 1974; Chiba and Cherniak, 1978). It is very likely that previous workers failed to recognize that benomyl is rapidly decomposed in organic solvents during normal analytical procedures, even though intact benomyl residues exist in or on plant tissues and in water (Chiba and Cherniak, 1978). Under these circumstances it is extremely important to elucidate the behavior of benomyl in water to study accurately the mode of action of this fungicide.

Chiba and Cherniak (1978) have reported that the reaction of decomposition of benomyl to MBC and BIC (n-butyl isocyanate) in different organic solvents is reversible, i.e., benomyl (k_{21}) ⇄ MBC + BIC (k_{12}). The results of their study showed that, in organic solvents such as chloroform, dichloromethane, ethyl acetate, benzene, ethanol, methanol, and dioxane, benomyl does not decompose completely to MBC and BIC, and due to the reversible nature of the degradation reaction, some percentage of benomyl always remains intact. However, Calmon and Sayag (1976b) reported that the conversion of benomyl to MBC in many organic solvents followed pseudo-first-order kinetics. Zweig and Gao (1983) reported that the decomposition of benomyl in acetonitrile followed first-order kinetics. According to the latter authors, a quantitative conversion of benomyl to MBC can be achieved in acetonitrile in approximately 3 h at 22 ± 1 °C for 10 mg L^{-1} benomyl solution.

Calmon and Sayag (1976a) also studied the kinetics of the conversion of benomyl to MBC in 50% v/v methanol and water using a spectrophotometric method and reported that the absorbance vs time plots gave pseudo-first-order rate constants graphically. Due to the low solubility of benomyl in pure aqueous media, these authors had to use a mixture of aqueous buffers and methanol to dissolve larger amounts of benomyl in the working solution, required to study its decomposition kinetics by the spectrophotometric method.

No systematic study on the kinetics of benomyl decomposition in aqueous solutions without organic solvents has been reported in the literature. Since a knowledge of the stability of benomyl in water at different pH values is important not only to agricultural and

* Author to whom correspondence should be addressed.
‡ Present address: Central Analytical and Materials Characterization Laboratories, Metrology, Standards and Materials Division, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

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analytical chemists but also to plant pathologists, the objective of this paper was to use a relatively more sensitive reversed-phase high-performance liquid chromatographic (RP-HPLC) method (Singh and Chiba, 1985; Chiba and Singh, 1986) to study the kinetics of the conversion of benomyl to MBC in aqueous solutions of neutral and acidic pH. We were also interested in reinvestigating the decomposition of benomyl in acetonitrile which was reported to follow first-order kinetics, different from that reported for other organic solvents by Chiba and Cherniak (1978).

MATERIALS AND METHODS

Chemicals. Benlate 50% WP (Wilson Laboratories, Laval, Québec) was used as the source of benomyl. All other chemicals were of analytical reagent grade. Acetonitrile and methanol used were of HPLC grade from Caledon Laboratories, Ltd., Georgetown, ON L7G 4R9, Canada. Buffer solutions of pH 1–7 were prepared as follows: pH 1 with 0.2 M KCl (68 mL) and 0.2 M HCl (182 mL); pH 3 with 0.1 M citric acid (159 mL) and 0.2 M Na_2HPO_4 (41 mL); pH 5 with 0.067 M Na_2HPO_4 (2.4 mL) and 0.067 M KH_2PO_4 (97.6 mL); pH 7 with 0.067 M Na_2HPO_4 (122 mL) and 0.067 M KH_2PO_4 (78 mL).

HPLC. A Perkin-Elmer Series 3 equipped with a Perkin-Elmer LC-55-S detector at 220 and 286 nm was used at room temperature (21 ± 1 °C).

Column. A Regis HiChrom reversible column, with 5-μm Spherisorb ODS (C-18) 15 cm × 4.6 mm (i.d.), and a Phenomenex ODS2 (C-18) 15 cm × 4.6 mm (i.d.) column were used.

Injector. A Rheodyne syringe loop type injector was used with a 50-μL loop.

Mobile Phase. The following mixtures were prepared: CH_3CN–H_2O–buffer (pH 7) (A) 40:45:15 v/v, (B) 50:46.5:3.5 v/v, and (C) 60:30:10 v/v. Each phase was run isocratically.

Flow Rate. Flow rates of 0.8–1.5 mL min^{-1} were used.

Procedure. Two methods were used to analyze benomyl in different aqueous buffers and organic solvents. In the first method, benomyl was directly analyzed by using mobile phases B and C. The decrease in benomyl peak height with time was used to calculate the kinetic rate constants (k) according to the equation

$$k = \frac{2.303}{\Delta t} \log \frac{C_1}{C_2} \quad (1)$$

where C_1 is the benomyl peak height at time t_1, C_2 is the benomyl peak height at time t_2, and $\Delta t = t_2 - t_1$.

The k values so calculated at different time intervals compared well (within 10%), thereby confirming the first-order rate kinetics. The confirmation of first-order rate kinetics was also derived from the linearity of the plots of log (peak height of benomyl) against time (graphic method).

In a second method known as the STB method (Chiba and Singh, 1986), benomyl was analyzed as STB as follows: 70 mL of the sample solution was treated with 5 mL of 2 M NaOH to convert benomyl to STB (3-butyl-2,4-dioxo-s-triazino[1,2-a]-benzimidazole). After 20 min, the solution was neutralized by adding 5 mL of 2 M HNO_3, and 5 mL of pH 7 buffer was added. Ten milliliters of CH_3OH and 5 mL of CH_3CN were also added to make the solvent composition of the sample and standards the same. In the STB method, the decrease in the STB peak height with time was used to calculate k. Working solutions were prepared by suspending WP 50% Benlate in different aqueous solutions for ~30 min. These solutions were filtered through the membrane filters to get clear solutions which were then analyzed by the RP-HPLC methods (as discussed above) at different time intervals. Weighed amounts of benomyl were dissolved in CH_3OH or CH_3CN for the kinetic studies in these solvents. Solubility of benomyl at different pH values was determined as reported earlier (Singh and Chiba, 1985).

RESULTS

Kinetic Study of Benomyl Decomposition in Aqueous Media. The rate constants of benomyl conversion to MBC in aqueous solution of different pH values, as determined by the RP-HPLC method, are listed in Table I. On the basis of our previous studies (Singh and Chiba, 1985; Chiba and Singh, 1986) and the retention time, it was confirmed that the decomposition product was MBC only, under the experimental conditions used. Unlike the case with organic solvents (Chiba and Cherniak, 1978), benomyl was decomposed consistently to MBC in aqueous solutions as illustrated in Table II. The degradation reaction followed first-order kinetics since the plots of log (peak height of benomyl) versus time showed linear relationship with coefficients of correlation ranging from 0.996 to 0.999.

Table I. Observed First-Order Rate Constants (k) for Benomyl Decomposition to MBC at 21 ± 1 °C in Aqueous Buffers and Solutions of Different pH Values

solvent	pH	approx benomyl concn, mgL^{-1}	k, s^{-1}	$t_{0.5}$, h
buffer	7.0	0.4	2.9×10^{-5}	6.6
distilled water	6.2	1.0	3.7×10^{-5}	5.2
1.0 M KCl	6.0	1.0	2.8×10^{-5}	6.9
0.1 M KCl	6.0	1.0	3.4×10^{-5}	5.7
buffer	5.0	3.6	2.5×10^{-5}	7.7
0.1 M KCl + 0.0001 M HCl	4.1	1.0	3.2×10^{-5}	6.0
0.1 M KCl + 0.001 M HCl	3.1	1.0	3.6×10^{-5}	5.3
buffer	3.0	4.0	3.2×10^{-5}	6.0
0.1 M KCl + 0.01 M HCl	2.1	1.5	3.1×10^{-5}	6.2
0.1 M HCl	1.1	6.0	1.2×10^{-5}	16.0
buffer	1.0	18.2	1.0×10^{-5}	19.3

Table II. Results of a Typical Kinetic Experiment of the Decomposition of Benomyl (~6.0 mg L^{-1}) to MBC in 0.1 M HCl at 21 ± 1 °C As Studied by RP-HPLC in Terms of Benomyl Peak Height

time, min	peak height, cm	k,[a] s^{-1}
12	16.1	
		1.2×10^{-5}
1270	6.3	
		1.2×10^{-5}
1400	5.8	
		1.4×10^{-5}
1460	5.5	
		1.1×10^{-5}
1820	4.3	
		1.2×10^{-5}
5520	0.30	
mean		1.2×10^{-5}
SD		1.3×10^{-6}
%RSD		10

[a] The value of k by graphical method was 1.2×10^{-5} s^{-1}.

Table II shows the results of typical kinetic experiments in 0.1 M hydrochloric acid. The k values were calculated by using eq 1. The mean k value of 1.2×10^{-5} was identical with the value determined by the graphical method. In 0.1 M hydrochloric acid a trace concentration of benomyl was detected even after 4 days. This shows that benomyl was more stable at pH 1.0. The value of $t_{0.5}$ at pH 1.0 was about 3 times greater than those at pH values between 2 and 7 (Table I). Similar behavior of benomyl degradation at different pH values was reported by Calmon and Sayag (1976a) in 50% v/v methanol and aqueous buffers.

The results shown in Figure 1 reveal that a relatively concentrated solution of benomyl may be prepared by dissolving it in 0.1 M (or higher) hydrochloric acid. These acidic solutions of benomyl will be more stable than the solutions prepared at less acidic and neutral pH values. The stability of benomyl dissolved in acid can be increased further by storing them at lower temperatures as $t_{0.5}$ values reported by Northover and Chiba (1989) for the

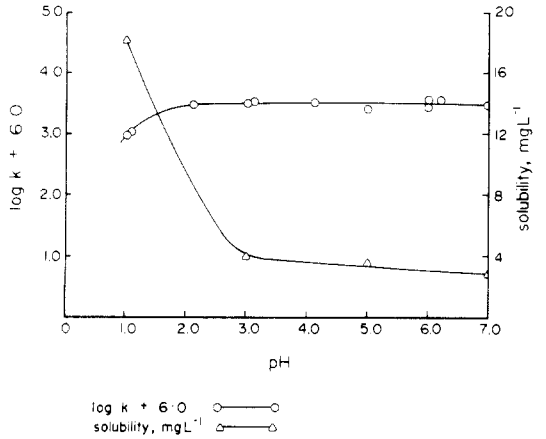


Figure 1. Plots of benomyl solubility and log k (rate constant) plus 6.0 for its decomposition to MBC versus pH of aqueous solutions.

Table III. Decomposition of Benomyl (~10 mg L^{-1}) to MBC in Acetonitrile at 21 ± 1 °C As Studied by RP-HPLC

time, min	peak height, cm	k_1,[a] s^{-1}	peak height − 2.0,[b] cm	k_2,[c] s^{-1}
9	15.8		13.8	
		2.1×10^{-4}		2.4×10^{-4}
21	13.6		11.6	
		2.0×10^{-4}		2.5×10^{-4}
59	8.6		6.6	
		1.7×10^{-4}		2.5×10^{-4}
109	5.2		3.2	
		1.4×10^{-4}		2.6×10^{-4}
152	3.6		1.6	
		8.5×10^{-5}		
212	2.7			
		1.3×10^{-5}		
507	2.1			
4166	2.0			
5760	2.0			

[a] k_1, rate constant based on peak height. [b] Peak height at equilibrium was 2.0 cm. [c] k_2, rate constants based on peak height minus peak height at equilibrium (2.0 cm), mean $k_2 = 2.5 \times 10^{-4} \pm 1 \times 10^{-5}$ s^{-1}.

decomposition of benomyl in water were about 40 times greater at 1 °C compard to those at 25 °C.

Kinetic Study of Benomyl Decomposition in Acetonitrile. Table III shows data on the decomposition of benomyl in acetonitrile. As shown, the rate constants at different time intervals (reported as k_1), calculated by using eq 1 do not show approximate constancy similar to that observed in aqueous media. This is because the conversion of benomyl to MBC is not complete in acetonitrile, as reported by Chiba and Cherniak (1978) for other organic solvents. The results of this study proved that the conversion of benomyl to MBC and BIC (butyl isocyanate) in acetonitrile was also reversible, as was the case in other organic solvents (Chiba and Cherniak, 1978). At equilibrium, about 12% benomyl remained intact. This contrasts with the results reported by Zweig and Gao (1983), who claimed to achieve complete conversion of benomyl to MBC in about 3 h. Further confirmation of the reversibility of benomyl degradation in acetonitrile can be derived from the peak of intact benomyl in the chromatogram (Figure 2) of a solution initially containing approximately 10 mg L^{-1} benomyl after 4 days. Equilibrium was achieved in approximately 8 h.

The kinetics of benomyl degradation in acetonitrile was also studied at 8 and 100 mg L^{-1} initial levels of benomyl by the STB method at 25 °C. The results of these experiments, together with the results from direct benomyl

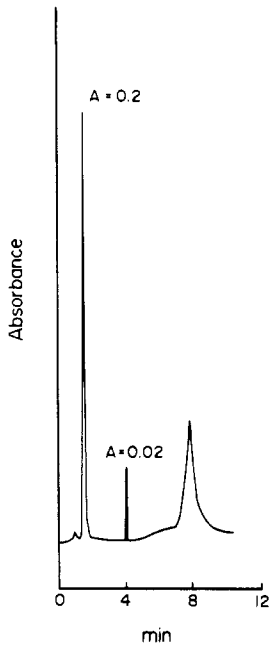


Figure 2. Chromatogram of benomyl in acetonitrile (prepared at 10 mg L^{-1} initially) after 4 days at 21 ± 1 °C. Peaks at RT of 1.5 and 8.0 min are MBC and benomyl, respectively.

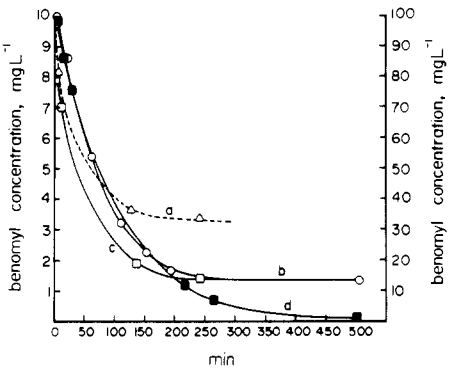


Figure 3. Decomposition kinetics of benomyl to MBC in acetonitrile and methanol. (a) 100 mg L^{-1} benomyl in acetonitrile; (b) 10 mg L^{-1} benomyl in acetonitrile, (c) 8 mg L^{-1} benomyl in acetonitrile; (d) 10 mg L^{-1} benomyl in methanol. Note that for (a) concentrations refer to the ordinate on the right-hand side (0–100 mg L^{-1}).

analysis, are plotted in Figure 3. Again, about 100% benomyl at the 8 mg L^{-1} level and about 30% at the 100 mg L^{-1} level remained intact. Clearly, the percentage of intact benomyl in acetonitrile at equilibrium was higher for more concentrated solutions. This is in accordance with the results reported by Chiba and Cherniak (1978) for chloroform.

It was possible to calculate the rate constant for the forward decomposition reaction after the absorbance at inifinite time (equilibrium) was subtracted from the absorbance at time t by using spectrophotometric methods, as reported by Calmon and Sayag (1976a). In the same manner, by subtracting the peak height of benomyl at equilibrium from the peak heights at different time intervals we calculated the rate constants for benomyl decomposition in acetonitrile. These results, illustrated in Table III, indicate the applicability of the RP-HPLC method in evaluating the kinetic rate constants of forward reaction of benomyl decomposition in organic solvents. Some authors in the past (Kirkland et al., 1973; Spittler et al., 1984) have used methanol and its mixture with hydrochloric acid for quantitative conversion of benomyl to MBC. Keeping this in mind, we have also studied the

Table IV. Observed Rate Constants (k) of Benomyl Decomposition to MBC at 21 ± 1 °C in Acetonitrile (CH_3CN), Methanol (CH_3OH), and Their Mixtures with Aqueous Solutions

solvent	approx benomyl concn, mg L^{-1}	k, s^{-1}	$t_{0.5}$, h
CH_3CN	10	2.5×10^{-4}	0.77
CH_3CN[a]	8	3.3×10^{-4}	0.58
CH_3CN[a]	100	3.0×10^{-4}	0.64
v/v, 20% pH 7 buffer + 80% CH_3CN	8	9.1×10^{-5}	2.1
v/v 50% pH 7 buffer + 50% CH_3CN	5	6.2×10^{-5}	3.1
pH 7 buffer	0.4	3.2×10^{-5}	6.0
CH_3OH	10	1.6×10^{-4}	1.2
v/v 17% H_2O + 83% CH_3OH	8	5.3×10^{-5}	3.6
v/v 50% H_2O + 50% CH_3OH	5	2.9×10^{-5}	6.6
H_2O	4	2.8×10^{-5}	6.9
v/v 17% 1 M HCl + 83% CH_3OH	8	1.4×10^{-5}	13.8

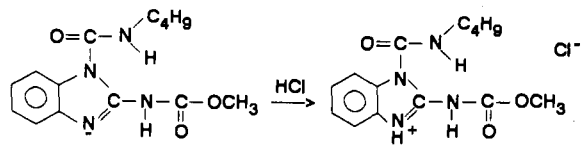
[a] CH_3CN, k was determined by the STB method at 25 °C.

kinetics of benomyl decomposition in pure methanol and mixed methanol–aqueous and acetonitrile–aqueous solutions. The results of these studies are reported in Figure 3 and Table IV.

DISCUSSION

Calmon and Sayag (1976a) studied the kinetics of the conversion of benomyl to MBC and reported that the reaction is due to spontaneous intramolecular catalysis. However, their kinetic studies were limited to a 50% v/v methanol–aqueous medium, due to the low solubility of benomyl in pure aqueous media. Although Peterson and Edgington (1969) mentioned that benomyl broke down to MBC in aqueous solution within 4 days, there appears to be no systematic study of this decomposition reaction in pure aqueous medium reported in the literature. The main reason for this may be due to the limitation of the spectrophotometric method in measuring the low concentration of benomyl in water. In the present paper, with the aid of a sensitive and more accurate RP-HPLC method (Singh and Chiba, 1985; Chiba and Singh, 1986), it became possible to study the kinetics of degradation of benomyl in pure aqueous media. The method was found to be accurate and reasonably reproducible with a relative standard deviation around 10%.

The kinetic results from aqueous solutions reported in Table I indicated that $t_{0.5}$ values for the degradation of benomyl were 5–8 h between pH values of 2 and 7. In addition, unlike the case with organic solvents (Chiba and Cherniak, 1978), the reaction in aqueous media followed first-order kinetics; i.e., benomyl was completely decomposed to MBC. This may be due to the hydrolysis of BIC in water. The reaction seems to have little dependence on the ionic strength and buffer components. At low pH (approximately pH 1) the decomposition of benomyl to MBC is slowed down. This decrease in the rate constant at low pH corresponded to an increase in the benomyl solubility. It seems, as also reported by Calmon and Sayag (1976a), that benomyl is protonated in acidic solutions (at pH <2) according to the reaction



It is very likely that in acid media the protonation of benomyl prevents the hydrogen bonding between the ring nitrogen and the proton of the amine group in the butylcarbamoyl moiety and stabilizes benomyl against intramolecular catalysis, responsible for benomyl degradation to MBC (Calmon and Sayag, 1976a). This protonation may explain the increase in solubility of benomyl at low pH, as shown in Figure 1. One of the main advantages of this finding may be that benomyl can be prepared in high concentration in aqueous acidic solution and, at the same time, can be stabilized due to the acidity of medium. Benomyl dissolved in these solutions should remain intact for a longer period of time if stored at low temperatures, i.e., at 1 °C or lower. Thus, it may be possible to make standards of known benomyl concentration in water for its quantification in aqueous medium. In the past, benomyl has generally been determined only as MBC after deliberate conversion because it was understood that it is impossible to determine intact benomyl in aqueous media. In the conversion method, however, it is impossible to differentiate newly converted MBC from MBC which had been present as a natural degradation of benomyl or thiophanate methyl.

The RP-HPLC method can also be used to determine the rate constant for the forward reaction of benomyl degradation to MBC and BIC in organic solvents as illustrated in Table III. In most organic solvents the degradation reaction is reversible, as characterized by Chiba and Cherniak (1978), who calculated rate constants for the forward and backward reactions. Calmon and Sayag (1976b) and Zweig and Gao (1983) have also determined the rate constant for benomyl degradation in organic solvents, which compared well with the values reported by Chiba and Cherniak (1978). However, using their approach, one cannot be sure about the reversibility of the reaction, or of the concentration of intact benomyl remaining at equilibrium, since these authors expected quantitative conversion of benomyl to MBC in organic solvents. In the present studies a reinvestigation of benomyl decomposition in acetonitrile (confirmed at three different levels of benomyl by using two analytical methods) has clearly indicated that the conversion of benomyl to MBC is not quantitative and, depending upon the initial level, some percentage of benomyl always remains intact. Thus, the RP-HPLC method can predict the behavior of benomyl degradation in organic solvents more accurately than spectrophotometric methods unless the approach suggested by Chiba and Cherniak (1976) is used.

The degradation of benomyl to MBC in methanol was found to be quantitative (Figure 3), thus making this solvent more appropriate for quantiative conversion of benomyl to MBC. The decomposition reaction followed first-order rate kinetics. This may be due to the reaction of BIC with methanol, thereby preventing the backward reaction, BIC + MBC → benomyl (Chiba, 1977). From Table IV it is clear that the degradation of benomyl slows down as the water concentration is increased in acetonitrile and methanol. The degradation of benomyl was even slower in acidified methanol (83% MeOH and 17% 1 M HCl). This mixture of methanol and hydrochloric acid was used by Kirkland et al. (1973) and Splittler et al. (1984) for quantitative conversion of benomyl into MBC which, on the basis of our present investigation, should be less effective as compared to pure methanol for the quantitative conversion of benomyl to MBC. This again shows that degradation of benomyl slows down in acidic medium.

CONCLUSION

The kinetics of benomyl degradation in aqueous solutions in the absence of organic solvents has been reported for the first time. The results clearly indicate that the degradation of benomyl in water is 6 and 9 times slower than in methanol and acetonitrile, respectively. The $t_{0.5}$ values of about 7 h at neutral pH show that the degradation of benomyl in water is not as rapid as previously believed (Clemons and Sisler, 1969). Stable benomyl solutions can be prepared by dissolution of benomyl in acid. The development of an analytical method to determine intact benomyl in surface water and drinking water is currently in progress and will be reported at a later date.

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