this temperature, structural changes in the clay reduced adsorption by reducing the surface area available for adsorption.

In aqueous solutions an inverse relationship was found between the adsorption of parathion and the release of parathion from highly loaded clays under equilibrium conditions.

The presence of an organic cation on the clay's surface altered the clay's behavior in aqueous solution, favoring increased adsorption and decreased desorption.

The results indicate that pretreatment of the clay can affect the rate of pesticide release and the amount released to the external environment.

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Kinetic Study of Reversible Conversion of Methyl 1-(Butylcarbamoyl)-2-benzimidazolecarbamate (Benomyl) to Methyl 2-Benzimidazolecarbamate (MBC) and *n*-Butyl Isocyanate (BIC) in Organic Solvents

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The decomposition of benomyl (B), methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, in chloroform, dichloromethane, ethyl acetate, benzene, ethanol, methanol, and dioxane was studied spectrophotometrically at 25 °C. The mechanism of decomposition in all the solvents is represented by: B (k_{21}) $\rightleftarrows$ MBC + BIC (k_{12}) where MBC is methyl 2-benzimidazolecarbamate and BIC is *n*-butyl isocyanate. Values of the specific rates k_{12} and k_{21} have been obtained for all the solvents studied. The values of k_{12} show no correlation with existing solvent parameters, but k_{21} values seem to be larger for less polar solvents. Kinetic and spectrophotometric evidence for the establishment of equilibrium has been obtained and the values of the equilibrium constant K seem to be larger for more polar solvents. Also, the largest value of the percentage of intact benomyl at equilibrium is found for benzene while the smallest value is found for methanol. The significance of these kinetic studies to the meaningful analysis of benomyl is discussed.

The fungicide benomyl (methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate) is reported to be unstable in aqueous media and breaks down rapidly to methyl 2-benzimidazolecarbamate (MBC) (Clemons and Sisler, 1969; Peterson and Edgington, 1970). Baude et al. (1973), however, demonstrated by using ^{14}C-labeled benomyl that benomyl is rather stable in water and on plants after application. Chiba and Doornbos (1974) reported a rapid degradation of benomyl in organic solvents and its degradation product was confirmed to be MBC. At the 170th National Meeting of the American Chemical Society in Chicago, 1975, Chiba reported that the degradation of benomyl is very fast in organic solvents when the solution is prepared, but the reaction soon reaches equilibrium. The degradation in water, on the other hand, is rather slow and is influenced by agents employed to disperse benomyl in water. Chiba concluded that the generally accepted view that benomyl rapidly degrades in water may not be correct. Previous workers had failed to recognize that benomyl is rapidly decomposed in organic solvents during ordinary extraction procedures even though intact benomyl residues existed in or on plant tissues and in water.

According to Austin et al. (1976) the solubility of benomyl in water was 3.8 ppm at 20 °C and the half-life of

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the dissolved benomyl was more than 7 h. Thus, when benomyl is suspended in water at a practical agricultural level of 250 ppm, all the chemical does not dissolve immediately and does not degrade rapidly.

Calmon and Sayag (1976) studied the kinetics of conversion of benomyl to MBC and reported that the reaction is due to spontaneous intramolecular catalysis. They obtained first-order rate constants for degradation but without taking into account the reversible nature of the reaction. In extending his study of 1975, Chiba developed a rapid and comprehensive spectrophotometric method of analysis (1977a) in which *n*-butyl isocyanate (BIC) was extensively used to control the reversible reaction: benomyl $\rightleftarrows$ MBC + BIC.

Kinetic studies, which take account of reaction reversibility, have now been performed. The results of these studies, which provide specific rates for benomyl degradation and reformation as well as equilibrium constants, are reported and the significance of these results to the practical analysis of benomyl are discussed.

MATERIALS AND METHODS

Chemicals. *Benomyl.* Recrystallized benomyl obtained from Benlate 50% WP was used. The purity of this benomyl was as good as recrystallized benomyl, obtained from E.I. du Pont de Nemours & Co., Inc.

MBC. Recrystallized MBC was also produced from Benlate 50% WP.

Solvents. Methanol, benzene, ethyl acetate, dioxane, and chloroform (without preservative) were "distilled-in-glass" grade from Burdick & Jackson Laboratories, Inc. Methylene chloride was "distilled-in-glass" grade from Caledon Laboratories Ltd. Absolute ethanol was from Consolidated Alcohols Ltd. It should be noted that a number of these solvents are on the NIOSH 1976 Subfile of Suspected Carcinogens.

Instrument. A Cary 14 spectrophotometer equipped with a deuterium lamp was used with jacketted Hellma silica cells of 1 cm light path. Temperature of the cell was controlled at 25 ± 1 °C with a Haake Type F constant temperature water circulator.

Spectrophotometric Procedures. The maximum absorbance of benomyl (λ max) exists at 294.7 nm. In chloroform, 10 and 25 ppm solutions were measured at this wavelength. For higher concentrations, different wavelengths were chosen: 298.5 nm for 50 ppm, 299.4 nm for 75 ppm, and 300.0 nm for 100 ppm solutions, respectively.

As soon as each solution was prepared, the absorbance (A) was continuously recorded at the specified wavelength. For the studies of degradation in different solvents, 294.7 nm was used and all the benomyl solutions were prepared at 10 ppm. Absorbances were continuously recorded similarly.

Kinetic studies. The basis for our kinetic studies and analyses was as follows: The rate law for benomyl (k_{21}) $\rightleftarrows$ MBC + BIC (k_{12}) is:

$$\frac{-\mathrm{d}(B_o - X)}{\mathrm{d}t} = k_{12}(B_o - X) - k_{21}X^2 \qquad (1)$$

where B_0 is the initial benomyl concentration (mol/L), X is the change in B_0 after a time t, and k_{12} and k_{21} are specific rates of benomyl degradation and reformation, respectively.

The integrated form of the rate law is:

$$\frac{X_e}{2B_o - X_e} \ln \frac{B_o X_e + X(B_o - X_e)}{B_o(X_e - X)} = k_{12}t \qquad (2)$$

where X_e, the equilibrium concentration of MBC and of BIC, is obtained from the condition $k_{12}(B_o - X_e) = k_{21}X_e^2$.

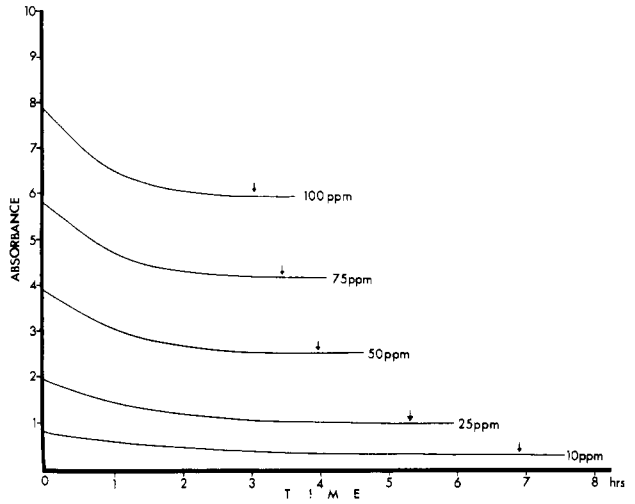

Figure 1. Time dependence of A (294.7 nm) for solutions of benomyl in chloroform for various initial benomyl concentrations (B_o, ppm): T = 25 ± 1 °C, path length = 1 cm.

On assuming the following Beer–Lambert conditions for a 1 cm path length:

$$A_o = \epsilon_B B_o \qquad (3)$$

$$A = \epsilon_B(B_o - X) + \epsilon_M X \qquad (4)$$

$$A_e = \epsilon_B(B_o - X_e) + \epsilon_M X_e \qquad (5)$$

where A_0, A, and A_e are zero time, time t, and equilibrium solution absorbances, respectively; ϵ_B is the zero-time extinction coefficient of undissociated benomyl; and ϵ_M is the extinction coefficient of MBC. The integrated form of the rate law becomes:

$$\theta = \frac{A_o - A_e}{A_o(1 - 2\beta) + A_e} \ln \left[\frac{A_o(1 - \beta)}{A - A_e} - \frac{(A - \beta A_o)(A_e - \beta A_o)}{A_o(1 - \beta)(A - A_e)} \right] = k_{12}t \qquad (6)$$

where $\beta = \epsilon_M/\epsilon_B$.

Except for values of t at which $A \sim A_e$, values of θ, the left-hand side of eq 6 vs. t were plotted to yield a B_0 or A_0 independent slope k_{12}. Once equilibrium is attained measurement of A_e values yield the equilibrium constant K:

$$K = \frac{k_{12}}{k_{21}} = \frac{X_e^2}{B_o - X_e} = \frac{(A_o - A_e)^2}{\epsilon_B(1 - \beta)(A_e - \beta A_o)} \qquad (7)$$

from which values of $k_{21} = k_{12}/K$ are obtained.

RESULTS AND DISCUSSION

Relationships between absorbance values at 294.7 nm and time for chloroform solutions containing different initial concentrations of benomyl are shown in Figure 1. It is clear that solutions of benomyl in chloroform obey the Beer-Lambert law. After times t_e denoted by ↓, there is no further change in absorbance; at that point it becomes time independent. If benomyl was completely and irreversibly converted to MBC and BIC then the absorbance of the solution at t_e would be given by $\epsilon_M B_0$ and the ratio A_0/A_e would equal $1/\beta$, since solutions of MBC in chloroform are also known to obey the Beer–Lambert law. These constant values of $\epsilon_M B_0$ and $1/\beta$ were not obtained, however, indicating that there were variable percentages of intact benomyl still remaining at individual equilibrium points.

Table I. Rates of Degradation and Reformation of Benomyl in Chloroform at 25 ± 1 °C

Benomyl concn						
ppm	Mol/L	k_{12}, s^{-1}	k_{21}, M^{-1} s^{-1}	K, M	Time to reach equilibrium (t_e), h	Intact benomyl remaining at equilibrium, %
10	3.43×10^{-5}	8.78×10^{-5}	1.47	5.98×10^{-5}	6.9	29.0
25	8.58×10^{-5}	9.50×10^{-5}	1.62	5.86×10^{-5}	5.3	44.6
50	1.72×10^{-4}	9.05×10^{-5}	1.57	5.76×10^{-5}	4.0	56.5
75	2.57×10^{-4}	9.13×10^{-5}	1.70	5.37×10^{-5}	3.5	63.6
100	3.43×10^{-4}	8.93×10^{-5}	1.69	5.27×10^{-5}	3.1	67.9
Av		9.08×10^{-5}	1.61	5.65×10^{-5}		

Table II. Rates of Degradation and Reformation of Benomyl (B_0 = 10 ppm = 3.43×10^{-5} mol/L) in Different Solvents at 25 ± 1 °C

Solvent	β	k_{12}, s^{-1}	k_{21}, M^{-1} s^{-1}	K, M	Time to reach equilibrium, (t_e), h	Intact benomyl remaining at equilibrium, %
Benzene	0.0877	1.91×10^{-4}	6.75	2.83×10^{-5}	3.7	41.5
Chloroform	0.155	0.88×10^{-4}	1.47	5.98×10^{-5}	6.9	29.0
Methylene chloride	0.0931	1.29×10^{-4}	1.44	8.93×10^{-5}	6.4	22.9
Ethyl acetate	0.0897	4.38×10^{-4}	1.81	2.42×10^{-4}	2.8	11.3
Ethanol	0.176	2.99×10^{-4}	0.722	4.14×10^{-4}	4.3	7.2
Dioxane	0.0698	3.31×10^{-4}	0.547	6.05×10^{-4}	4.0	5.2
Methanol	0.186	2.69×10^{-4}	0.0505	5.33×10^{-3}	5.6	0.6

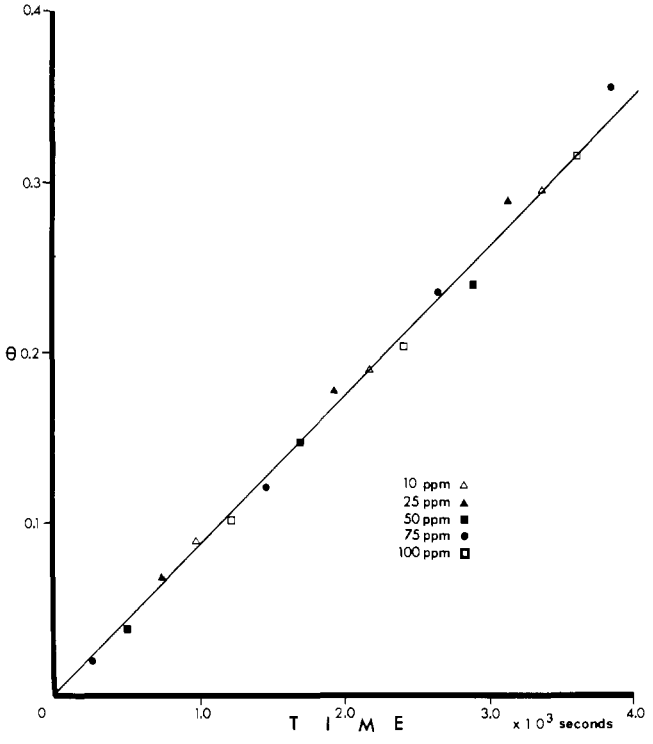

Figure 2. Plot of values of (θ) in function 6 vs. time for solutions of benomyl in chloroform: B_0 = 10, 25, 50, 75, and 100 ppm; T = 25 ± 1 °C, path length = 1 cm.

Figure 2 is the plot of values of θ in expression 6 vs. time for all the solutions referred to above. It can be seen that an excellent linear plot is obtained (correlation coefficient = 0.997) with B_0 independent slope $k_{12} = 9.02 \times 10^{-5}$ s^{-1} at 25 ± 1 °C.

Table I summarizes the data obtained on the individual solutions of benomyl in chloroform by using expressions 6 and 7. The percentage of intact benomyl remaining at equilibrium was calculated from:

$$\frac{100B_e}{B_0} = \frac{100(A_e - \beta A_0)}{A_0(1-\beta)} \quad (8)$$

where $B_e = B_0 - X_e$ is the equilibrium concentration of benomyl. It is apparent that the degradation of benomyl in chloroform is represented by benomyl (k_{21}) $\rightleftharpoons$ MBC + BIC (k_{12}). Plots similar to Figure 1 obtained for benomyl

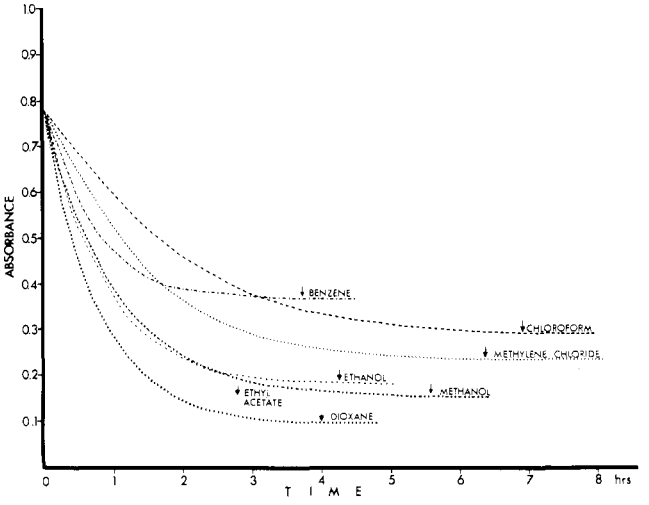

Figure 3. Time dependence of A (294.7 nm) for solutions of benomyl (B_0 = 10 ppm) in benzene, chloroform, methylene chloride, ethyl acetate, ethanol, methanol, and dioxane: T = 25 ± 1 °C, path length = 1 cm.

(B_0 = 10 ppm) in various solvents at 25 °C are shown in Figure 3. On plotting the values of θ in expression 6 vs. time for each of these solutions, excellent linear plots were also obtained. Table II shows that degradation of benomyl in each of the solvents is also represented by benomyl (k_{21}) $\rightleftharpoons$ MBC + BIC (k_{12}). The data were obtained on solutions of benomyl in these solvents by using expressions 6 and 7.

While the values of k_{12} shown in Table II differ from those given by Calmon and Sayag (1976), they are similarly ranked and appear not to show any correlation with existing solvent parameters. On the other hand, larger k_{21} values are obtained for less polar solvents and large K values are obtained for more polar solvents, although dioxane seems to be an exception. Also, the largest percentage of intact benomyl at equilibrium is found in benzene while the smallest is found in methanol.

The above results are relevant to the performance of meaningful analyses for benomyl. For example, if a 1000 ppm solution is prepared in chloroform at 25 °C, the degradation of benomyl starts immediately and after a short time equilibrium is attained at which point 88% of the original benomyl remains intact. Therefore, if an analysis is made after equilibrium has been reached it will

appear that benomyl is stable in that solvent (Chiba, 1977a). The results of this study make it possible to correct for the degradation which has taken place in the solvents tested, with the possible exception of methanol.

Chiba (1977a) has used *n*-butyl isocyanate extensively in his spectrophotometric method for the analysis of benomyl. For example, benomyl standard solutions have been stabilized with 1000 ppm BIC in chloroform. The results of this study make it possible to determine the extent of stabilization. As an example consider a solution originally containing 10 ppm benomyl (3.43×10^{-5} mol/L) in chloroform. To reform benomyl from the MBC present, one portion of a chloroform solution containing 100 000 ppm BIC is added to nine portions of this sample. The resultant BIC concentration is 10 000 ppm (0.101 mol/L). The value of $X = 1.92 \times 10^{-8}$, the moles of benomyl decomposed per liter, is obtained from:

$$K = 5.65 \times 10^{-5} = \frac{X(X - 0.101)}{3.43 \times 10^{-5} - X} \simeq \frac{0.101X}{3.43 \times 10^{-5}} \quad (9)$$

Thus, 99.944% of intact benomyl remains in this solution.

Without the aid of BIC, it is difficult to retain intact benomyl in the solutions if concentrations of benomyl are low. For example, when benomyl solutions are prepared at 1 ppm and 0.1 ppm in chloroform, the percentage of benomyl remaining at equilibrium is calculated to be only 5.5 and 0.6%, respectively.

For the extraction of benomyl from different samples, ethyl acetate (Pease and Holt, 1971), benzene (Rouchaud and Decallonne, 1974), and chloroform (Peterson and Edgington, 1969, 1971) were used. Although the workers, who used ethyl acetate and benzene, did not intend to recover intact benomyl in their extracts and further treated the extracts with other chemicals, it is of value to know the exact status of solutes in the extract at the time of further chemical treatment.

As a result of this study, the behavior of benomyl in organic solvents has been well elucidated, particularly regarding the reversible reaction of benomyl to MBC + BIC. With the better understanding obtained from this study about the rate of degradation of benomyl in organic solvents and with the knowledge of the significant effect of temperature on the degradation (Chiba, 1977b), more accurate and comprehensive analysis of benomyl and MBC can be achieved by using Chiba's spectrophotometric method (1977a).

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Crystal and Molecular Structure of Organophosphorus Insecticides. 10. Chlorpyrifos

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The crystal and molecular structure of chlorpyrifos {*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl thiophosphate, $(H_5C_2O)_2P(S)OC_5NHCl_3$, monoclinic, $C2/c$, a = 22.06 (1), b = 9.485 (2), c = 15.990 (6) Å, β = 114.63 (4)°, Z = 8, Mo Kα radiation} has been determined by three-dimensional x-ray analysis. The structure was solved by conventional Patterson and Fourier techniques to a final discrepancy index R = 0.066 for 1421 observed reflections ($|F_o| > 2.5\sigma(F_o)$). The phosphorus–meta hydrogen distance of 5.78 Å is within the range of literature values cited for insect acetylcholinesterase (AChE), yet is well outside that for mammalian AChE. CNDO molecular orbital charge density calculations and van der Waals arguments are presented to correlate the solid state structure to a probable in vivo model.

The crystal structure investigation of chlorpyrifos was undertaken as a part of a study of various organophosphorus (OP) insecticides being carried on at this laboratory (Baughman and Jacobson, 1975; Gifkins and Jacobson, 1976; Rohrbaugh and Jacobson, 1976; Baughman and Jacobson, 1976; Baughman and Jacobson, 1977; Rohrbaugh and Jacobson, 1977; Baughman et al., 1978; Baughman and Jacobson, 1978). The purpose of such a program is to better understand the relationship between structure and mechanism(s) relative to an insecticide's toxicity–activity. Ronnel, bromophos, Crufomate, and ronnel oxon (the first, fourth, sixth, and eighth references, respectively, above) are all *phenoxy* OP's. The study of heteronuclear ring systems was begun with azinphosmethyl and fospirate (third and fifth references) in order to note any conformational similarities and/or dissimi-

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