90% of the ^{14}C was recovered as butralin (based on TLC evidence). For trifluralin at the first week sampling time, there was a major difference in volatile products recovered between the light and dark flasks. About 90% of the ^{14}C was recovered as trifluralin in the dark, but only 25.3% in the light. Most of the ^{14}C (72.6%) was located in more polar products than trifluralin at or adjacent to the origin on the TLC plate in the uv experiments. At subsequent sampling dates the relative amount of photoalteration decreased with a larger percentage of the volatilized ^{14}C appearing as trifluralin.

This fairly simple system appears to offer a mechanism for simultaneously measuring volatility and CO_2 metabolic loss of pesticides on or in soils. Before the system can be applied to other pesticides, the trapping characteristics of the plugs should be tested. The system was easy to maintain although the soils lost moisture during the time between weekly samplings. The use of humidified air may control or prevent soil moisture loss. Studies on vapor phase photolysis may be feasible in the system, although considerable difficulty was experienced in identifying any trifluralin photoproducts when the plug extracts were examined by GLC–mass spectral analysis.

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Instability of Methyl 1-(Butylcarbamoyl)-2-benzimidazolecarbamate (Benomyl) in Various Solvents

In all the solvents investigated, the conversion of benomyl to MBC proceeds by spontaneous intramolecular catalysis. The observed rate constants show no correlation with the existing empirical solvent parameters but can be explained in terms of solvent–solute interactions. Spontaneous intramolecular catalysis is markedly slowed down by water.

The systemic fungicide, benomyl, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, is unstable in dilute aqueous solutions and is rapidly converted into methyl 2-benzimidazolecarbamate (MBC) by removal of the butylcarbamoyl side chain (Clemons and Sisler, 1969). Benomyl is soluble in some organic solvents (Du Pont de Nemours and Co., 1970; Pease and Holt, 1971) but its stability is not well documented in spite of the work done (Kilgore and White, 1970; Chiba and Doornbos, 1974). The kinetic study we carried out allowed us to elucidate the effect of various solvents on the conversion rate of benomyl.

EXPERIMENTAL SECTION

Apparatus. A Unicam SP 800 recording spectrophotometer, equipped with a thermostated multiple cell compartment, was used for all spectroscopic measurements.

Chemicals. All organic solvents were analytical grade materials. Benomyl was supplied by Du Pont de Nemours-France. MBC was obtained through hydrolysis of benomyl; its chemical characteristics were identical with those reported in the literature.

Uv Spectra. Water–methanol solutions of benomyl and MBC exhibited the following absorptions [λ_{max} nm (log ϵ); s = shoulder]: benomyl, 223 (4.3), 240 (4.0), 255 (3.9), 263 (3.9) s, 285 (4.2) s, 294 (4.3); MBC, 241 (4.0), 281 (4.1) s, 287 (4.2), 294 (3.8) s.

Kinetic Measurements. All reactions were carried out at 25 ± 0.1°C in tightly stoppered 1-cm quartz cells. The change in optical density of the substrate was followed at suitable wavelengths. Initial repetitive scans of the uv region established that these reactions held tight isosbestic points, indicating the absence of intermediates.

The absorbance vs. time plots gave the pseudo-first-order rate constants graphically, using the experimental infinity value. The observed rate constants k_{obsd} were obtained by plotting log $(A_t - A_\infty)$ vs. time, where A_∞ and A_t are the absorbance readings at infinity and at time t, respectively: $\log (A_t - A_\infty) = \log A_0 - (k_{obsd}/2.303)t$.

RESULTS AND DISCUSSION

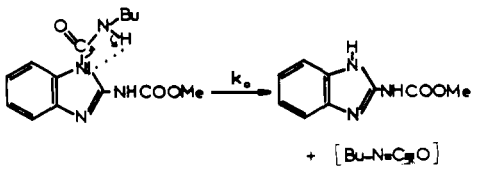
The constants derived from the kinetic study of the solvolysis of benomyl in various solvents at 25 ± 0.1°C are listed in Table I.

The investigation of the uv spectra recorded at the end

Table I. Solvolysis Rates for Benomyl at 25°C

Solvent	$k_{obsd} \times 10^4$, s^{-1}
H_2O-MeOH (1:1, v/v)	0.45
MeOH	2.50
EtOH	3.03
PrOH	2.61
i-PrOH	2.92
n-BuOH	2.23
i-BuOH	1.57
sec-BuOH	2.30
t-BuOH	1.73
$CHCl_3$	0.84
1,4-Dioxane	3.72
AcOEt	5.40
MeCN	3.38
Me_2SO	4.10

Scheme I



of reaction shows that, in every solvent studied, the final product is methyl 2-benzimidazolecarbamate (MBC). Therefore, it is sound to think that the reaction mechanism involves a spontaneous intramolecular catalysis, as previously evidenced in acidic and neutral media (Calmon and Sayag, 1976). The formation of an H-bond between the hydrogen of the nitrogen of the butylcarbamoyl side chain and the lone pair of the nitrogen atom N_1 of the benzimidazole ring leads to a four-membered ring, which, being unstable, opens and yields methyl 2-benzimidazolecarbamate and butyl isocyanate (Scheme I).

Organic solvents belong to three main groups (Parker, 1962): neutral solvents (hydrocarbons and chlorine-containing solvents) have very low dielectric constants; intramolecular interactions are restricted to van der Waals forces; protic solvents (water, alcohols, carboxylic acids) have a proton which can form an H-bond with molecules having a lone pair of electrons (ketones, ethers, alcohols); chloroform is intermediate between neutral and protic solvents; dipolar aprotic solvents (acetone, acetonitrile, dimethyl sulfoxide) have in their molecules areas of high electronic density, which give them a high solvation power.

The kinetic data obtained for the solvolysis of benomyl clearly show no correlation with well-defined physical or chemical parameters such as the solvent dielectric constant, its dipole moment, or its basicity. A fairly large number of semiempirical parameters are often successfully applied to account for the various interaction mechanisms between solvent and solute molecules (Reichardt and Dimroth, 1968; Fowler et al., 1971); the dielectric function K of Kirkwood, the solvent-induced frequency shift E of Reichardt and Dimroth, the square root δ of the cohesive energy density of Herbrandson and Neufeld, which all show good correlations with the observed rate constants for unimolecular reactions, are of no use here.

As a first approximation, the kinetic data for the solvolysis of benomyl can be explained qualitatively in terms of interactions between solute and solvent molecules.

In a polar solvent, such as dimethyl sulfoxide, the benomyl molecule is hydrogen bonded (most likely through NHCOOMe) to the solvent sulfonyl oxygen atom (structure I). Spontaneous intramolecular catalysis will then be enhanced as the nitrogen atom N_1 of the benzimidazole ring becomes more negative.

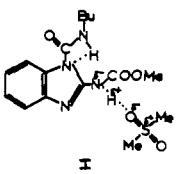
When the solvent is less polar (as is $CHCl_3$), this kind

Table II. Rates of Hydrolysis for Benomyl in Various Water-Methanol Mixtures

Solvent	$k_{obsd} \times 10^4$, s^{-1}
MeOH	2.50
MeOH-H_2O (90:10, v/v)	1.59
MeOH-H_2O (80:20, v/v)	1.10
MeOH-H_2O (70:30, v/v)	0.74
MeOH-H_2O (60:40, v/v)	0.54
MeOH-H_2O (50:50, v/v)	0.45

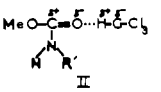
Table III. Rates of Hydrolysis for Benomyl in Me_2SO-MeOH-H_2O Mixtures

Solvent	Mole fraction × Me_2SO	$k_{obsd} \times 10^4$, s^{-1}
Me_2SO	1	4.09
Me_2SO 50% v	0.260	2.37
Me_2SO 25% v	0.092	0.997
Me_2SO 10% v	0.037	0.634
MeOH-H_2O (50:50, v/v)	0	0.486



I

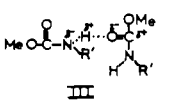
of interaction becomes less important (structure II, where



II

R' = 1-(butylcarbamoyl)benzimidazolyl).

In a nonpolar solvent, the association would be expected to be solute–solute intermolecular hydrogen bonding between NH and CO groups (structure III, where R' =



III

1-(butylcarbamoyl)benzimidazolyl).

Such modes of association are known for amide molecules of the type ROC(=O)N(HR') (Keith and Alford, 1970). Furthermore, benzimidazoles are known to associate through intermolecular hydrogen bonding as evidenced by their ir spectra (Rabiger and Joullie, 1964).

The behavior of water is rather peculiar; as a matter of fact, the observed rate constants in various water–methanol mixtures (Table II) show that the reaction velocity is rapidly decreasing as the water content of the mixture is increasing.

As benomyl is water insoluble, it has no affinity for this solvent; therefore, benomyl molecules do not associate with water molecules though water is a polar solvent. On the contrary, benomyl molecules associate with methanol molecules and much more with Me_2SO molecules, which results in a speeding up of the rate of intramolecular catalysis. In the case of mixed solvents, interactions between molecules are also involved; dimethyl sulfoxide "traps" water molecules. This is the reason why spontaneous intramolecular catalysis is faster in Me_2SO–(MeOH–H_2O) mixtures than in MeOH–H_2O mixtures.

The same phenomenon is observed when dimethyl sulfoxide and increasing amounts of a water–methanol (1:1,v/v) solution of pH 3.35 are mixed together (Table III).

CONCLUSIONS

This brief study of the solvolysis of benomyl points to the marked slowdown of intramolecular catalysis by water and to the associations between solvents and benomyl

molecules. The investigation of intramolecular reactions is of great importance because of their striking analogy with enzyme catalysis which proceeds through an enzyme–substrate complex. Imidazoles were the first organic bases whose catalytic role was evidenced in the hydrolysis of esters. Imidazole and its derivatives have been much studied because of the apparent involvement of the imidazolyl group of histidine at the active site of many hydrolytic enzymes such as chymotrypsin, trypsin, cholinesterase, or ribonuclease (Bruice and Benkovic, 1966).

Furthermore, the kinetic data reported above are of some practical value by allowing a better choice of solvents for analytical techniques (extraction, clean-up, chromatography, etc.) relative to benomyl determination.

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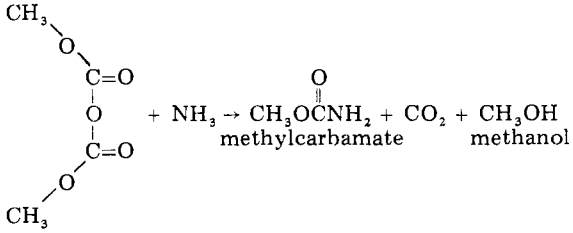
Measurement of Methylcarbamate Formed by the Addition of Dimethyl Dicarbonate to Model Solutions and to Wines

A method for ethylcarbamate analysis was adapted for detecting methylcarbamate formed from dimethyl dicarbonate added to solutions and wines containing varied amounts of ammonia and at different pH values. Recovery from wine by this method is 51%, less than found for ethylcarbamate in the original study. The effects of pH and NH_3 concentration on the amount of methylcarbamate formed are similar to those for ethylcarbamate. Under the most extreme conditions in normal commercial wine practices (pH $\leq$3.75, $NH_3 \leq 20$ mg/l.) less than 10 μg of methylcarbamate per l. would be formed from the addition of dimethyl dicarbonate at 100 mg/l.

Diethyl dicarbonate (DEDC) as an additive to wine has been discussed at some length in regard to the consequent formation of ethylcarbamate (Ough, 1976b). An additive which might be substituted for DEDC is the dimethyl dicarbonate (DMDC), a compound with similar fungicidal properties but resulting in methyl side products instead of ethyl compounds. The effectiveness of DMDC (Ough, 1975), the amount of methanol formed, and the methods of measuring it (Stafford and Ough, 1976) have been reported. The methylcarbamate is produced by the reaction of ammonia with the DMDC.



This work was done to determine whether the methylcarbamate forms in a manner similar to the formation of ethylcarbamate from DEDC and ammonia. Secondly, methods used to measure ethylcarbamate are applied to find how much methylcarbamate would be formed in wine.

METHODS AND MATERIALS

The equipment used was similar to that reported for measuring ethylcarbamate (Ough, 1976a). All the usual precautions were taken, as discussed previously. Pure methylcarbamate was obtained from Pfaltz and Bauer Inc. Experimental samples of DMDC were obtained from Logica International Corp. The samples were in excess of 99.5% pure by our analysis.

The ammonia content of the wines and buffer solutions was measured with a Beckman research pH meter and an Orion ammonia probe, Model 95-10.

The chloroform (Mallinckrodt, A.R.) and ethyl acetate (Mallinckrodt, A.R.) used were redistilled, and a 5% head and a 5% tails cut removed. All other reagents, reagent grade or better, were used as received. Solvent blanks showed no detectable peak at the retention time of methylcarbamate.

Total phenols and pH were determined as given by Amerine and Ough (1974).

Model solutions were prepared by combining appropriate volumes of 0.1 M dibasic potassium phosphate and 0.2 M citric acid, both in 11% v/v ethanol, and diluting to volume with 11% v/v ethanol (1 part buffers + 3 parts ethanol solution). Ammonia was added as $(NH_4)_2SO_4$, and final pH adjustments were made with concentrated NaOH or H_2SO_4. DMDC was added by the appropriate microliter syringe. Samples were allowed to stand at 20 °C for at least 24 h before extraction and analysis. The analytical procedure was similar to that reported for model solution and wine analysis for ethylcarbamate (Ough, 1976a). The model solutions were extracted with ethyl acetate. Extracts of model solutions were concentrated and analyzed directly. The chloroform extracts of the wines were purified on Florisil PR 60/100, and the eluate was concen-