Effects of Temperature on the Equilibrium of Benomyl, and Its Degradation Products Methyl 2-Benzimidazole Carbamate and n-Butyl Isocyanate in Benzene and Chloroform

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

Rapid degradation of benomyl to methyl 2-benzimidazol carbamate (MBC) in common organic solvents has been reported by Chiba and Doornbos (1974). Calmon and Sayag (1976) confirmed this finding and calculated the rate of degradation. They stated that "the conversion of bemomyl to MBC proceeds by spontaneous intramolecular catalysis" and "the observed rate constants show no correlation with the existing empirical solvent parameters but can be explained in terms of solvent-solute interactions". Chiba (1975) recently reported that n-butyl isocyanate (BIC), one of the degradation products of benomyl, is the key substance that controls this reaction. He extended this finding and developed a simple spectrophotometric method to determine benomyl and MBC simultaneously in solvent systems. He also reported that degradation of benomyl to MBC in common organic solvents stops at certain equilibrium points.

This paper demonstrates the effect of temperature on rate of degradation of benomyl and its equilibrium concentration in two commonly used solvents.

MATERIALS AND METHODS

Chemicals - Benomyl (recrystalized) was obtained from E.I. DuPont de Nemours and Co., Inc. Solvents used were benzene (Caledon Laboratories Ltd.) distilled in glass, and chloroform (BDH), Analar grade.

Procedure - To determine the effect of treatment and temperature on the benomyl concentration in benzene and chloroform several experiments were run. The necessary standard curves were prepared and analyses were conducted according to the methods of Chiba (1975). All benomyl solutions used were prepared at the concentration of 10 ppm. At the beginning of each experiment and at different points throughout, the percentage of intact benomyl remaining in solution was determined. A Beckman DK-2A ratio recording spectrophotometer with

Bulletin of Environmental Contamination & Toxicology,
Vol. 18, No. 3 © 1977 by Springer-Verlag New York Inc.

near IR-silica cells (1 cm light path) was used for all such measurements.

Generally 50 ml portions of the benomyl solutions were subjected to the various experimental conditions. When a solution was blended, the 50 ml portion was placed in a 60 ml container (Omni-Mixer, Ivan Sorvall, Inc., Norwalk, Conn., U.S.A.) and blended for 15 min to simulate the procedure for residue extraction. Extractions were conducted either in an ice water bath or without temperature control. Some solutions were held at 25°C (room temperature) with gentle shaking or no agitation. Temperatures of other solutions with no agitation were controlled in either a refrigerator or water bath with a temperature controller (Fail Safe Temp Unit, Techne Cambridge Ltd., Duxford, Cambridge, England).

RESULTS

Table 1 shows that a much smaller proportion of intact benomyl remained in both benzene and chloroform after high speed blending than after gentle shaking. When the benzene solution was blended for 15 min the temperature of the solution was 52°C. It declined to 45°C by the time absorption had been measured; the percentage of benomyl that remained intact at that point was 27%. The effect of blending on degradation of benomyl was more evident in chloroform than in benzene where only 15% of the benomyl remained intact after blending.

TABLE 1

Percentage of benomyl remaining intact in benzene and chloroform after 15 min of either blending or gentle shaking.

	Blending		Shaking	
Solvent	% remaining	temp °C[a]	% remaining	temp °C[b]
Benzene	27	52(45)	76	25
Chloroform	15	59(50)	92	25

[a] Solution temperature after 15 min blending; the figure in () is the temp 4 min after blending stopped.

[b] Room temperature, 19 min after the original solution was prepared.

Temperature proved to be the factor that accelerated degradation. When a benzene solution was subjected to the same mechanical blending, but temperature was controlled at 6°C in an ice water bath, the proportion of benomyl remaining intact was identical to that of solutions kept without agitation in a refrigerator at the same temperature (Fig. 1, A, B). In contrast, the temperature of the benzene solution, blended at 25°C without temperature control, increased to 52°C (Table 1). Although the temperature dropped quickly to 25°C the percentage of intact benomyl remained much lower (Fig. 1, D) than that in the solution held throughout at 25°C (Fig. 1, C). A very similar sequence to Fig. 1 D was followed with another solution which was held at 50°C for 25 min without agitation and subsequently held at 25°C (Fig. 1, E).

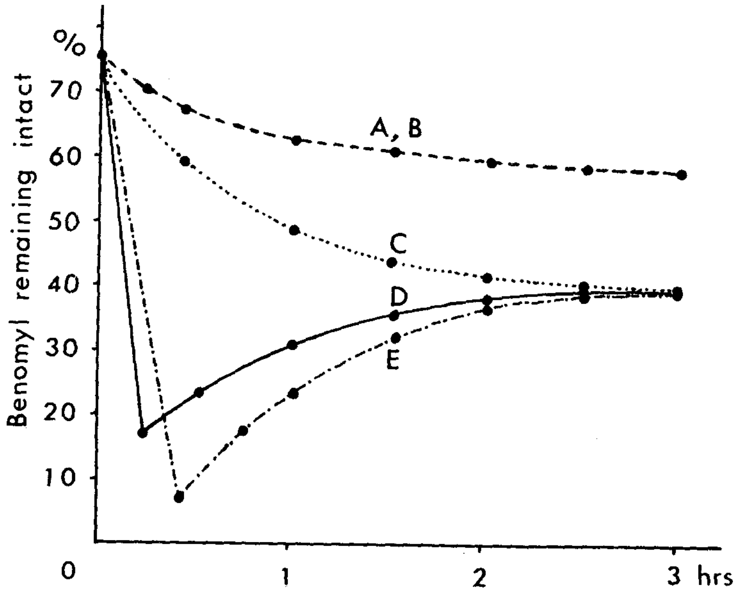

Fig. 1. Percentages of benomyl remaining intact in benzene solution (initial concentration 10 ppm) after different treatments: A) No agitation at 6°C; B) Blended for 15 min in an ice water bath and subsequently held at 6°C; C) No agitation at 25°C; D) Blended for 15 min without temperature control and subsequently held at 25°C; E) Held at 50°C for 25 min with no agitation and subsequently held at 25°C.

The percentages of benomyl remaining intact in a chloroform solution, which was blended for 15 min and subsequently held at room temperature, were essentially identical to those in the comparable solution held without agitation at 50°C for 15 min and subsequently held at room temp (Fig. 2, B, C). It took almost 4 hrs for the heated solution to return to the equilibrium expected at room temperature (Fig. 2, A). When the solution was held at 40°C, the rate of degradation of benomyl was much faster than at 25°C; the percentages of benomyl remaining at the equilibrium point were 9% (Fig. 2, D) and 24% (Fig. 2, A), respectively.

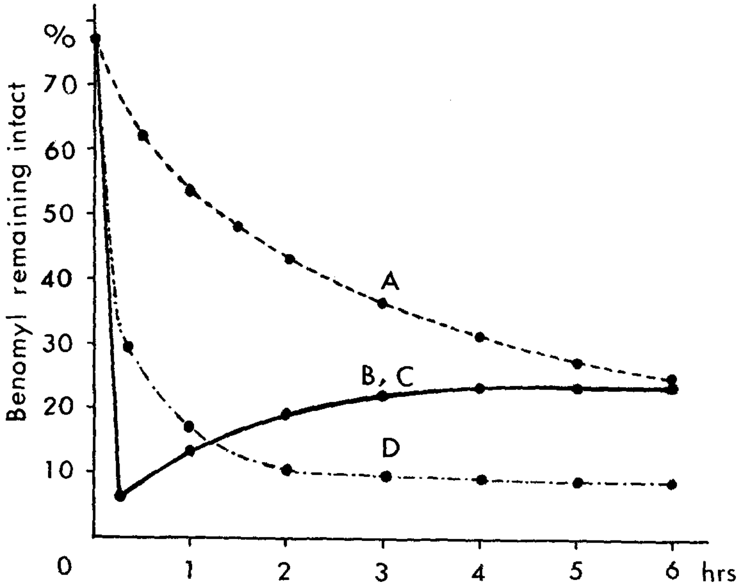

Fig. 2. Percentages of benomyl remaining intact in chloroform solution (initial concentration 10 ppm) after different treatments: A) No agitation at 25°C; B) Blended for 15 min without temperature control and subsequently held at 25°C; C) Held at 50°C for 15 min with no agitation and subsequently held at 25°C; D) No agitation at 40°C.

The proportion of benomyl remaining intact over the temperature range of 25-60°C was higher in benzene than in chloroform (Fig. 3). At 25°C, the proportions of intact benomyl after equilibrium had been reached were 40% and 24% in benzene and chloroform respectively. For both solvents, the proportion of benomyl in the system decreased significantly as the temperature increased. Practically no benomyl remained in chloroform at 60°C.

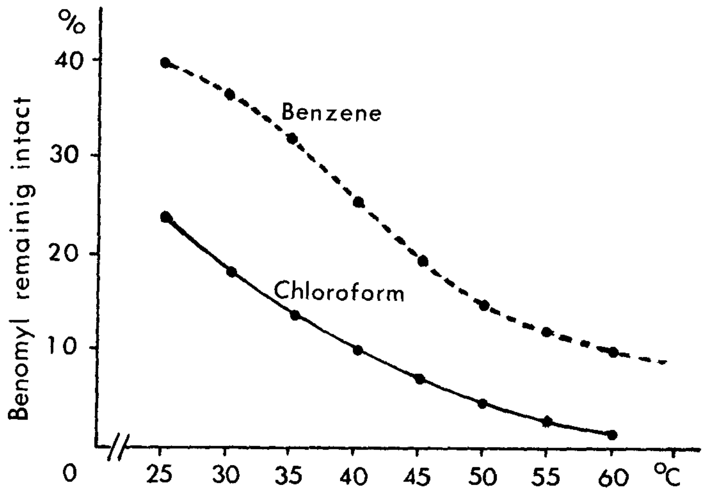

Fig. 3. Percentage of benomyl remaining intact in benzene and chloroform solutions (initial concentration 10 ppm) relative to temperature.

DISCUSSION

At present the only method available for determining intact benomyl at the ppm level is that reported by Chiba (1975) which uses UV absorption of benomyl at 294 mu and 286 mu. Use of a high speed blender is not recommended in this method because pigments and other co-extractives interfere with spectrophotometric determination. From the present study it is clear also that blending is undesirable because of the degradation of benomyl resulting from the temperature rise.

At a constant concentration, temperature proved to be the sole factor that affected the equilibrium point between benomyl and its decomposition products, MBC and BIC. Mechanical agitation had no effect. Benomyl was reformed slowly at room temperature from the MBC and BIC formed at higher temperatures. The rate of the reaction to reform benomyl is affected significantly, however, by the concentration of BIC as demonstrated by Chiba (1975).

The results of this study indicate that a large percentage of benomyl is degraded during the blending procedure because of the heat generated. Hence, it is essential to maintain a constant low temperature during extraction if individual concentrations of intact benomyl and MBC are to be determined rather than the total of the two.

ACKNOWLEDGEMENT

The author wishes to thank R.G. Richards for his technical assistance.

REFERENCES

CALMON, J.P., D.R. SAYAG: J. Agric. Food Chem. 24, 426 (1976).

CHIBA, M.: Rate of degradation of benomyl in common organic solvents and water. Presented at the 170th American Chemical Society National Meeting, Chicago, August, 1975.

CHIBA, M., F. DOORNBOS: Bull. Environ. Contam. Toxicol. 11, 273 (1974).