LABORATORY EVALUATION OF SEMIOCHEMICAL DISPENSERS: A THEORETICAL CHEMICAL KINETIC APPROACH TO THE EMISSION RATE OF DISPARLURE ACTIVE INGREDIENT

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Abstract

Emission rate of active ingredient is a critical factor to affect efficacy of semiochemical dispensers in pest management. From an insect pest management standpoint, it is desirable to have a device that could release the semiochemical at a constant rate. In practice, such a device may be difficult to realize. Capillaries as controlled-release devices have been developed since 1980. However, many of reports indicated that pheromone-charged fibers used commercially in insect control strategies performed in poor agreement with the predicted release rate (Weatherston et al. 1985a, Weatherston et al. 1985b). Currently, the most popular and economical semiochemicals release vehicles are still the classical controlled-release devices, such as plastic, rubber, laminate, microcapsules, rope, etc. Measuring vapor phase (absorbate analysis) and examining the residual content (weight loss or solvent extraction analysis) of the samples exposed in the laboratory or the field are the widely used methods to obtain the emission rate. However, the disadvantage of these classical methods is time consuming, requiring months or years to get the results (Warthen et al. 1998a, Warthen et al. 1998b). Sometimes the determination is difficult, e.g., determining emission rates at below room temperature.

In order to quickly obtain the emission rate at any temperature and save the time, a theoretical chemical kinetic approach has been deployed. It is hypothesized that volatile active ingredients are desorbed from absorbent type controlled-release devices following first order kinetics ($-dc/dt = kc$), which is proved to be valid for acetates and alcohols in polyethylene tubing (Bradley et al. 1995, McDonough et al. 1992) and rubber septa dispensers (McDonough 1991). This hypothesis was tested in this study using seven different disparlure formulations including three commercial disparlure formulations from Hercon Environmental Inc. (flakes and laminate tape), one from Trécé Inco. (string), three formulation from Shin-Etsu Chemical Co., Ltd., and one laboratory made red natural rubber septum formulation at six different temperatures (50, 55, 60, 65, 70, and 75 °C) in the oven for 4 days. The airflow through the system was maintained at 10 L/min by a valve on the hose vacuum source and the airspeed over the dispensers within the oven chamber was calculated to be 0.32 cm/sec. Three samples from each temperature were taken out every 24 h, extracted with certain amount of solvent for 48 h, and the amount of residual disparlure was determined by a capillary GC.

Experimentally it was found that first-order hypothesis was valid to all tested formulations. When the function percentage concentrations of disparlure determined at different temperature were plotted against the function time the exponential decay curves ($C/C_0 = e^{-kt}$) were displayed. After logarithm transformation ($\ln C/C_0 = -kt$), the straight lines were obtained with the linear regression coefficients, R^2, about 0.9. The rate constants (k) at each temperature and each formulation can be obtained from the slopes of each line.

An important property of a first-order kinetic is the half-life time ($t_{1/2}$). That is the time required for the concentration of disparlure to decrease to half its initial value. Half-life time ($t_{1/2}$) of first-order kinetics is independent on concentration. In all of other order kinetics, half-life time ($t_{1/2}$) is the function of concentration. So that the rate constant (k) of first-order kinetics can be obtained by an equation: $k = 0.693/t_{1/2}$, or half-life time ($t_{1/2}$) can be obtained by an equation: $t_{1/2}= k/0.693$.

The relation between the rate constant (k) and absolute temperature (T) was first proposed by Arrheniuis:

$$k = Ae^{-E/RT}$$

Where: A = *frequency factor* R = *gas constant*
E = activation energy T = absolute temperature
Activation energy of each formulation can be obtained from equation, ln $k = -E/RT + A$. If the function ln k for various temperatures is plotted against the function 1/T, the activation energy (E) is equal to the slope of the straight line times the gas constant R (Fig. 1). After determination of activation energy (E), the rate constant (k) at any temperature can be calculated by Arrheniuis equation: ln $k_2/k_1 = E/R\ (T_2\text{-}T_1/T_2T_1)$, and the longevity of the formulation, half-life time ($t_{1/2}$), can be easily obtained (Fig. 2 and 3).

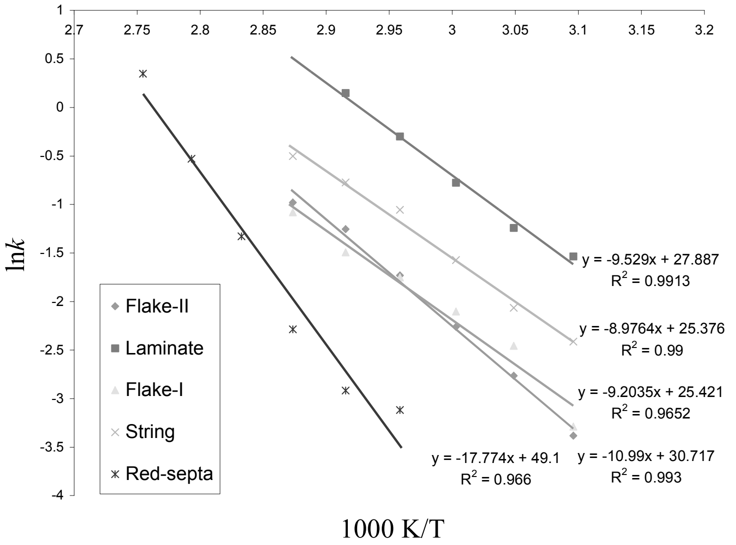

Figure 1.—Result of activation energy of disparlure dispensers (2003)

Overall, the apparent activation energies (E) and rate constants (k) of all tested dispensers have been determined based on experimental data, and therefore the longevities of the formulation, half-life time ($t_{1/2}$), at any different temperature can be calculated. The values of half-life time ($t_{1/2}$) of tested formulations are compatible to those obtained from green hose ageing study (Fig. 2 and 3). Therefore, these parameters can be used as standards to evaluate the dissemination of active ingredient from different semiochemical dispensers at different temperature conditions.

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Table 1.—Result of disparlure emission rate study (2003)

Dispenser	$t_{1/2}$ (day)			
	Kinetic			Green House
	15 °C	25 °C	35 °C	
Laminate (500 µg)	136	45	16	
String (500 µg)	244	86	32	
Flake (I) (200 µg)	398	136	50	67
Flake (II) (200 µg)	1,155	320	97	99
Red Septa (1000 µg)	210,000 (575Y)	23,650 (72Y)	3,777 (10Y)	

Table 2.—Result of disparlure emission rate study (2004)

	Kinetic		Green House	
Dispenser	R^2	$t_{1/2}$*	R^2	$t_{1/2}$**
Flake (I) (172 µg)	0.9523	101	0.7051	102
Shin-Etsu A (123 µg)	0.9922	58	0.9772	80
Shin-Etsu C (76 µg)	0.9776	34	0.9753	62
Shin-Etsu NI (97 µg)	0.8634	39	0.8494	86

R^2= liner regression coefficient
*half-life time (day, 25 ^{0}C, calcul.)
** half-life time (day, 27 ^{0}C, obser.).