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## Equilibrium and Kinetics of Desorption of Picloram and Parathion in Soils

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The desorption of picloram from Palouse silt, parathion from Panoche clay loam, and parathion from Palouse silt loam was investigated using a flow system. The desorption-kinetic reaction constant,  $k_0'$ , was calculated from the specific desorption,  $(x/m)_d$ , as a function of time. The  $k_0'$  values at 25 °C are 0.457, 0.099, and 0.011 for the above three soil-pesticide systems, respectively. Activation parameters for each system were evaluated. The activation energy,  $E_a$ , is 8.6, 8.2, and 3.0 kcal/mol for these three systems, respectively. The standard enthalpy for the equilibrium adsorption is compared with the enthalpies of activation for the kinetic adsorption and desorption processes. The interpretation of the activation parameters for each system was supplemented by X-ray diffraction data. Hypotheses concerning the mechanisms involved in the desorption process for these chemicals in these soils are discussed.

Parathion (*O,O*-diethyl *O*-(*p*-nitrophenyl) phosphorothioate) is a very effective insecticide and larvicide. A concentration of 0.01 ppm is sufficient to control mosquito larvae (Yasuno et al., 1966). Depending on the method of application, a good portion of the insecticide deposits on the soil. Residues in soil are subjected to desorption by water and lead to contamination of other components in the ecosystem. Nicholson et al. (1962) recovered 1.7 ppm parathion by weight from a soil in a peach orchard 9 months after the last application and 1.9 ppm was recovered from the bottom soil of a pond located in this orchard, yet a maximum concentration of 3 ppb is recommended for reservoir water (Malov, 1957). Using a batch technique, Saltzman et al. (1972) examined the adsorption and desorption of parathion in soil. The authors found that organic matter played an important role in retaining the parathion.

The utilization of picloram (4-amino-3,5,6-trichloropicolinic acid) as a potent herbicide has been recognized (Laning, 1963; Hamaker et al., 1963; Hoffman, 1971). Its resistance to degradation in the environment ranks next to the chlorinated hydrocarbons (Hiltbold, 1974) and could pose some environmental danger even though it is relatively nontoxic to many animal species (Lynn, 1965). Davidson and Chang (1972) investigated the movement

of picloram in soil as related to soil bulk density, particle size, and pore-water velocity.

Since the behavior of pesticides in soil is largely a dynamic phenomenon, a study of the interaction parameters associated with adsorption and desorption is instructive. Often the rates of adsorption and desorption are more important in predicting the movement of a pesticide in soil than the equilibrium adsorption behavior. The present work examines the desorption of picloram and parathion from two soils employing a flow-type kinetic method. Desorption reaction constants were calculated from the experimental results, and their variation with temperature was used to calculate the activation energy and other activation parameters. The activation parameters are compared with the thermodynamic equilibrium parameters for the various systems. The thermodynamic data obtained were used to gain insight into the mechanisms of interaction of pesticides in soil.

### EXPERIMENTAL SECTION

**Materials.** All chemicals used were reagent or analytical grade. Solutions of picloram and parathion were prepared by procedures described in a previous paper (Biggar et al., 1978). The eluting or desorption solution was 0.01 M calcium chloride.

**Methods.** The apparatus and collection procedures of the desorption kinetic experiments were described elsewhere (Biggar et al., 1978). At the end of the kinetic adsorption experiment, the delivery tube-syringe assembly was separated from the upper fritted-glass top. The pesticide solution in the top was quickly emptied out and the top was rinsed twice and then filled up with the desorption solution. The pesticide solution retained by the soil did not flow out, and because of the fritted-glass

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partition, the soil column was not disturbed during this conversion process. The outside of the apparatus was wiped dry and immediately connected to a different delivery tube-syringe assembly which had been initially filled with the desorption solution. The time required for the whole conversion process was less than 45 s. The desorption experiment was started immediately by turning on the infusion pump, the fraction collector, and the time clock.

Three desorption systems were studied, each at 15, 25, and 35 °C: (a) picloram with Palouse silt loam (system Ib), (b) parathion with Panoche clay loam (system IIB), and (c) parathion with Palouse silt loam (system IIIb). (Subsequently, Palouse silt refers to Palouse silt loam and Panoche clay to Panoche clay loam.) Several flow rates of the desorption solution and two soil weights were used.

The effluent solution was analyzed by liquid scintillation (LS). The possibility of degradation of the chemicals in the effluent solution and in the soil was investigated by a GLC procedure described elsewhere (Biggar et al., 1978). No degradation was observed and the input radioactivity was quantitatively recovered from the effluent and soil.

**Calculation of the Specific Desorption at Various Times.** The amount of pesticide in micrograms collected in each effluent collection is  $t_iFC_i$ , where  $t_i$  is the duration of each collection (h);  $F$  is the flow rate of the desorption solution (mL/h);  $C_i$  is the concentration of the effluent solution in each collection ( $\mu\text{g}/\text{mL}$ ). The total amount of pesticide ( $\mu\text{g}$ ) collected in the effluent solution after  $n$  collections is  $\sum_{i=1}^n (t_iFC_i)$ . However, at the onset of the desorption experiment the soil column retained one pore volume  $V_0$  (mL) of pesticide solution at a concentration  $C_e$  ( $\mu\text{g}/\text{mL}$ ).  $C_e$  was either equal to  $C_0$  (the influent concentration of the pesticide during the adsorption portion of the kinetic experiment ( $\mu\text{g}/\text{mL}$ ), or very nearly equal to  $C_0$ . The amount of pesticide ( $\mu\text{g}$ ) initially present in the solution in contact with the soil is  $C_eV_0$ . The amount of pesticide desorbed after  $n$  collections is  $\sum_{i=1}^n (t_iFC_i) - C_eV_0 + C_nV_0$ , where  $C_n$  is the estimated concentration of the solution in the column at the time the  $n$ th collection is terminated. The specific desorption of the pesticide,  $(x/m)_d$ , is defined as  $[\sum(t_iFC_i) - C_eV_0 + C_nV_0]/m$ , where  $m$  is the weight (g) of the soil in the column.

**X-ray Diffraction Experiment.** The detailed method for the preparation of samples for X-ray diffraction studies is described elsewhere (Biggar et al., 1978). The 0.2–2  $\mu\text{m}$  fraction of a Na-saturated bentonite clay was reacted with picloram (system Ia), with picloram at pH 1.2 adjusted with HCl (system IIA), and with parathion (system IIIa). A portion of the clay suspension was filtered through a small piece of ceramic plate. After analysis by X-ray, a desorption experiment was performed by washing with distilled water the pesticide-clay sample on the ceramic plate ten times. The sample was oven-dried at 90 °C for 3 h and subjected again to X-ray analysis. Then it was washed with 1.0 N  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , dried, and once more analyzed by X-ray.

## RESULTS AND DISCUSSION

**Rate of Desorption.** Various flow rates  $F$  (or flux,  $f$ , which is proportional to  $F$ ) and two soil weights ( $m$ ) at various temperatures ( $T$ ) were used for the desorption kinetics experiments. Table I contains the experimental conditions of the kinetic runs. The kinetic data obtained from the desorption experiments when plotted according to eq 1 yielded a linear plot as exemplified by Figure 1 (a

$$\frac{1}{(x/m)_d} = \frac{k'}{t} + Q' \quad (1)$$

Table I. Kinetic Data for the Desorption Experiments

| $T, ^\circ\text{C}$         | $1/Q', \mu\text{g}/\text{g}$ | $F, \text{mL}/\text{h}$ | $m, \text{g}$ | $k_r'$ |
|-----------------------------|------------------------------|-------------------------|---------------|--------|
| Ib. Picloram and Palouse    |                              |                         |               |        |
| 15                          | 0.149                        | 0.458                   | 2.5           | 0.0125 |
| 15                          | 0.140                        | 1.15                    | 6.5           | 0.0123 |
| 15                          | 0.138                        | 1.15                    | 2.5           | 0.0410 |
| 15                          | 0.160                        | 2.29                    | 2.5           | 0.0720 |
| 15                          | 0.370                        | 1.15                    | 2.5           | 0.116  |
| 25                          | 0.272                        | 0.458                   | 6.3           | 0.0170 |
| 25                          | 0.300                        | 0.458                   | 2.5           | 0.0420 |
| 25                          | 0.115                        | 2.29                    | 6.3           | 0.0370 |
| 25                          | 0.325                        | 1.15                    | 6.3           | 0.0560 |
| 25                          | 0.170                        | 0.458                   | 2.3           | 0.0210 |
| 25                          | 0.123                        | 1.15                    | 6.2           | 0.0160 |
| 25                          | 0.139                        | 1.15                    | 2.5           | 0.0410 |
| 35                          | 0.088                        | 2.29                    | 6.5           | 0.0390 |
| 35                          | 0.084                        | 1.15                    | 2.7           | 0.0410 |
| 35                          | 0.086                        | 2.29                    | 2.7           | 0.104  |
| IIb. Parathion and Panoche  |                              |                         |               |        |
| 15                          | 23.0                         | 1.15                    | 2.9           | 1.786  |
| 25                          | 16.5                         | 2.29                    | 7.6           | 1.242  |
| 25                          | 3.5                          | 1.15                    | 2.9           | 0.427  |
| 25                          | 3.5                          | 4.58                    | 7.6           | 0.485  |
| 35                          | 2.95                         | 2.29                    | 2.9           | 1.015  |
| IIIb. Parathion and Palouse |                              |                         |               |        |
| 15                          | 52.                          | 4.58                    | 2.7           | 1.762  |
| 25                          | 40.                          | 4.58                    | 2.7           | 1.439  |
| 35                          | 37.                          | 1.15                    | 2.7           | 0.365  |
| 35                          | 34.                          | 4.58                    | 2.7           | 1.704  |

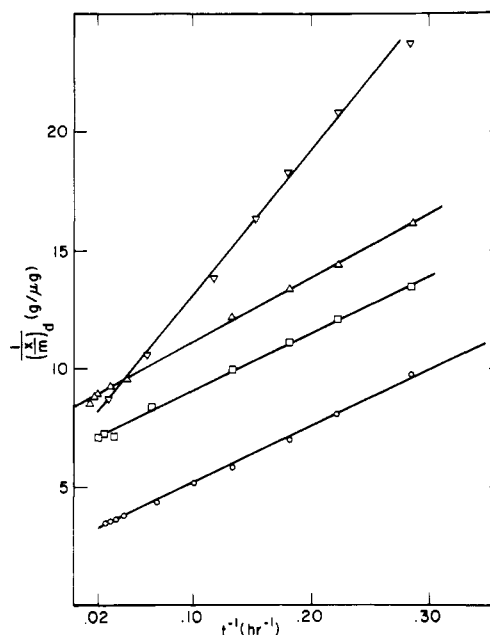


Figure 1. The reciprocal of the specific desorption  $(x/m)_d^{-1}$  vs. the reciprocal of time ( $t^{-1}$ ) for experiments in system Ib (Picloram and Palouse) at 25 °C. The symbols [O, □, Δ, ▽] refer to  $k_r'$  values of 0.042, 0.041, 0.037, and 0.016, respectively, in Table I.

minor qualification for system IIB is discussed below).

The functional dependence of  $(x/m)_d$  on  $t$  is the same as that of the specific adsorption on  $t$  (Biggar et al., 1978). Equation 1 can be rewritten in the following form:

$$(x/m)_d = \frac{t}{k' + Q't} \quad (2)$$

$$\lim_{k'/Q' \gg t} (x/m)_d = \frac{t}{k'} = k_r't \quad (2a)$$

$$\lim_{k'/Q' \ll t} (x/m)_d = \frac{1}{Q'} \quad (2b)$$

Thus, at small times the rate of desorption approaches a

Table II. Activation Parameters Associated with Desorption

| systems                     | $T, ^\circ\text{C}$ | $k_0'^a$            | $\Delta G'^{\ddagger}, \text{kcal/mol}$ | $\Delta S'^{\ddagger}, \text{cal mol}^{-1} \text{ deg}^{-1}$ | $\Delta H'^{\ddagger}, \text{kcal/mol}$ | $E_a', \text{kcal/mol}$ |
|-----------------------------|---------------------|---------------------|---|--|---|-------------------------|
| Ib. picloram and Palouse    | 15                  | $0.305 \pm 0.05$    | $0.712 \pm 0.09$                        | $25.3 \pm 2$   |   |                         |
|                             | 25                  | $0.457 \pm 0.06$    | $0.470 \pm 0.08$                        | $25.3 \pm 2$   | $8.0 \pm 1.$                            | 8.6                     |
|                             | 35                  | $0.740 \pm 0.07$    | $0.181 \pm 0.09$                        | $25.4 \pm 2$   |   |                         |
| IIb. parathion and Panoche  | 15                  | $0.0728 \pm 0.007$  | $1.572 \pm 0.05$                        | $20.9 \pm 2$   |   |                         |
|                             | 25                  | $0.0992 \pm 0.014$  | $1.386 \pm 0.08$                        | $20.9 \pm 2$   | $7.6 \pm 1.$                            | 8.2                     |
|                             | 35                  | $0.166 \pm 0.015$   | $1.077 \pm 0.05$                        | $21.2 \pm 2$   |   |                         |
| IIIb. parathion and Palouse | 15                  | $0.0112 \pm 0.0007$ | $2.695 \pm 0.04$                        | $-1.0 \pm 1$   |   |                         |
|                             | 25                  | $0.0119 \pm 0.0007$ | $2.659 \pm 0.04$                        | $-0.87 \pm 1$  | $2.4 \pm 1.$                            | 3.0                     |
|                             | 35                  | $0.0148 \pm 0.0012$ | $2.528 \pm 0.05$                        | $-0.42 \pm 1$  |   |                         |

<sup>a</sup> The uncertainties are derived from the uncertainties in the slope of the plot of  $1/(x/m)_d$  vs.  $1/t(k')$ ; see eq 1 and Figure 1.

constant  $k_r'$  while at large times the desorption approaches some limit ( $1/Q'$ ) and from physical considerations this limit must exist. It should equal (if no fixation occurred) the total amount adsorbed per gram in the adsorption experiment. At times approaching zero the rate of desorption is the rate of the pure desorption process at the surface concentration in equilibrium with  $C_e$  (or approximately  $C_0$ ). Thus, at the low concentrations studied  $k_r'$  is the desorption rate at steady state with the adsorption rate  $k_r$  as defined previously (Biggar et al., 1978). In system IIb the plot of  $(x/m)_d^{-1}$  vs.  $(t)^{-1}$  displayed some curvature at large  $t$ . This will not affect the following analysis of  $k'$  as equaling the inverse of the desorption rate at vanishing time since at small times the fit to a straight line was good (Figure 2). It can be shown that the desorption rate as  $t \rightarrow 0$  can be extracted from the data even if the functional dependence of  $(x/m)_d$  on  $t$  is not as defined in eq 1.

If the desorption process is a "unimolecular" process (i.e., a dissociation of an adsorbate-adsorbent complex), then as  $t \rightarrow 0$  when only desorption occurs we should have the relation

$$k_r' = \frac{d(x/m)_d}{dt} \quad (3a)$$

when  $t \rightarrow 0$

$$= \frac{K'F(1/Q')De^{-E_0'/RT}}{m} = k_0'F(1/Q')Dm^{-1} \quad (3b)$$

where  $E_0'$  is the activation energy for the desorption process,  $K'$  is a constant, and  $D$  is the ratio  $m/V_0$  where  $V_0$  is the pore volume of the column.  $D$  is a function of the type of soil and its packing in the column. The derivation of eq 3 is similar to that of eq 5 and 6 for adsorption (Biggar et al., 1978). The term  $(1/Q')D$  gives the amount of adsorbate adsorbed per  $1 \text{ cm}^3$  of solution in contact with the column. Thus  $k_0'$  is a rate constant for desorption equivalent to  $k_0$  defined for the adsorption process. The term  $F(1/Q')D$  equals the quantity of adsorbed molecules coming in contact with the desorption solution per unit time at  $t \rightarrow 0$ .  $k_0'$  as well as  $k_0$  are defined per unit concentration rather than activity. Hence, they are not strictly rate constants in the thermodynamic sense. Yet, at the low concentrations studied (and prevalent in natural systems), the neglect of activity coefficients is justified.

The values of  $k_r'$  for the three systems are contained in Table I. Indeed, it is observed that when the temperature ( $T$ ), flow rate ( $F$ ), and the weight of soil ( $m$ ) are constant, the values of  $k_r'$  are proportional to  $D/Q'$  or approximately proportional to  $1/Q'$  in a given soil. Similarly when  $D/Q'$ ,  $T$ , and  $m$  are held constant,  $k_r'$  is proportional to  $F$ . Maintaining the same  $T$  and  $F$ , and  $D/Q'$ , makes  $k_r'$  proportional to  $m^{-1}$ . All the results of the desorption

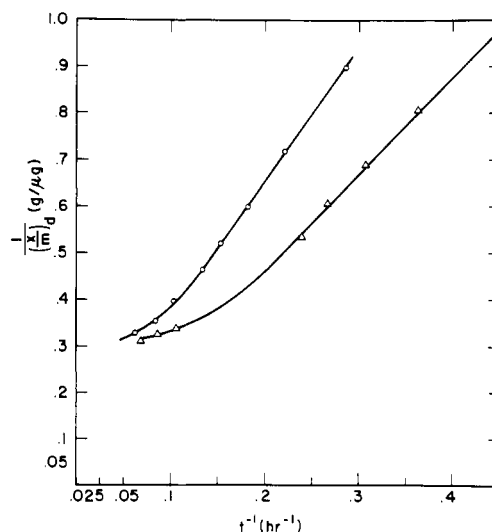


Figure 2. The reciprocal of the specific desorption  $(x/m)_d^{-1}$  vs. the reciprocal of time  $(t^{-1})$  for experiments in system IIb (Parathion and Panoche) at  $25^\circ\text{C}$ . The symbols  $[\Delta, \circ]$  refer to  $k_r'$  values of 0.485 and 0.427, respectively, in Table I.

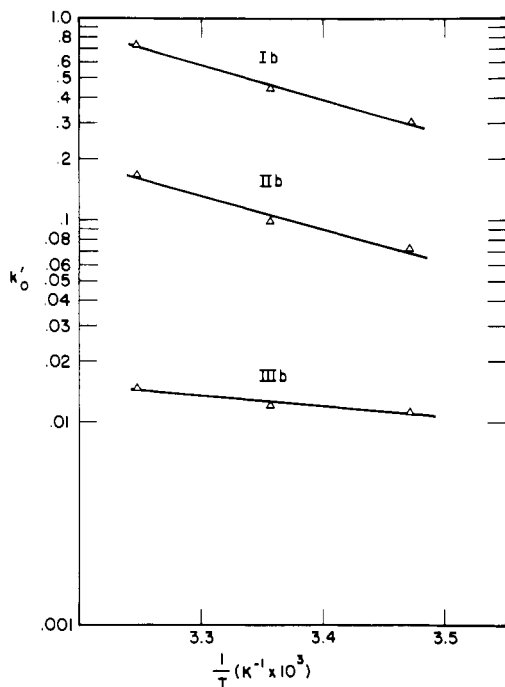
kinetic experiments, under various experimental conditions, can be interpreted in the same manner within experimental error. Thus, in agreement with eq 3, the value of  $k_r'$  is first order in  $F$  and  $D/Q'$  and inversely first order in  $m$ . The dimensionless desorption reaction constant  $k_0'$  can be defined from eq 3 as

$$k_0' = k_r' \frac{1}{F} m \frac{Q'}{D} \quad (4)$$

and is given in Table II. It is a measure of the intensity of the desorption for a given system and temperature.

**Activation Parameters Associated with the Desorption Kinetics.** Plots of  $\ln k_0'$  vs. the reciprocal of the absolute temperature  $1/T$ , for systems Ib, IIb, and IIIb are presented in Figure 3.

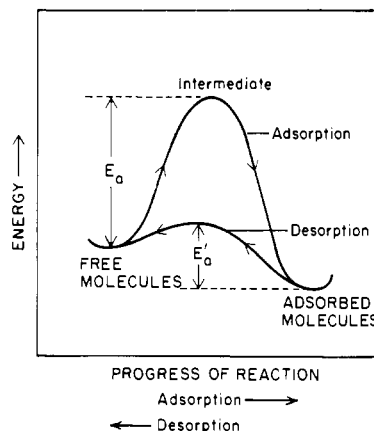
The linear relations indicate as suggested by eq 3 that temperature dependence of  $k_0'$  will yield the Arrhenius activation energy for desorption as well as the enthalpy of activation for desorption. The definitions and methods of calculations of the enthalpy of activation,  $\Delta H'^{\ddagger}$ , the entropy of activation,  $\Delta S'^{\ddagger}$ , the free energy of activation,  $\Delta G'^{\ddagger}$ , and the Arrhenius activation energy,  $E_a'$ , were described previously (Biggar et al., 1978). The values of these parameters are given in Table II, where the  $E_a'$  values for systems Ib and IIb are 8.6 and 8.2 kcal/mol, respectively. These energy levels are higher than those involved in hydrogen bonding (4–5 kcal/mol). In the desorption process, the pesticide molecules which were initially trapped in a potential well require input of energy for removal. For system Ib, the picloram molecules interact



**Figure 3.** The relation between the natural logarithm of the relative desorption constant ( $\ln k'_0$ ) and inverse of the absolute temperature  $1/T$ .

predominantly with the organic fraction (Biggar et al., 1978) through hydrogen bonding and chelation through a metal ion bridge mechanism (Biggar and Cheung, 1973). In the case of the system IIb the parathion molecules interact appreciably with both the organic and clay fractions (Biggar et al., 1978). In the case of system IIIb adsorption of parathion on the organic matter dominates. As discussed for the adsorption process the differences in behavior between systems IIb and IIIb may reflect the differences between adsorption of parathion on the clay and on the organic matter.

The  $E_a'$  value (3.0 kcal/mol) for system IIIb is low as compared with the other two systems. The adsorption-desorption process in system IIIb might be represented by an energy diagram given in Figure 4, relating the potential energy to the progress of the reaction. The adsorption reaction is presumably a continuous process involving a gradual transition from its free state to the adsorbed state (left to right in Figure 4). The desorption reaction is the reverse (right to left). The molecules undergo an intermediate state of reaction situated at the top of the hill in the energy diagram. The activation energy is the difference between the energy contents of the reactants and the intermediate. The desorption process in system IIIb involves a lower energy of activation than the adsorption (Biggar et al., 1978). This may be a result of the adsorbent-adsorbate complex being at a higher energy than the molecule in solution or (as assumed in Figure 4) the desorption may proceed via a different pathway than the adsorption, requiring a lower energy. This can happen, for example, if the adsorption requires removal of some species from the surface such as water molecules. The effect of moisture content on the rate of adsorption of parathion on soils can be inferred from reported studies (e.g., Yaron and Saltzman, 1972). The behavior of parathion on both soils suggests that parathion adsorption on clay may be described by trapping of the molecule in a potential well and desorption by escaping that well. With organic matter, parathion adsorption is dominated by the removal of water (yielding higher activation energy), and



**Figure 4.** A hypothetical energy diagram for the adsorption and desorption processes in system IIIb.

its desorption by a direct escape from the potential well at the surface rather than by exchange with water. Once the parathion is adsorbed it may be in such a conformation and position that it repels water and prevents the reverse of the exchange occurring during adsorption. Parathion is bulky enough and contains polar sites which may compete with water at the surface ( $\text{NO}_2$ ,  $\text{P}=\text{S}$ , etc.) and hydrophobic groups which may repel water if properly situated (e.g., alkyl groups).

The above discussion does not imply that the soil is a simple medium in which one adsorption or desorption mode exists. The activation parameters measured for a heterogeneous system such as soil generally represent either the dominant interaction or the average of several equally important interactions. They nonetheless provide insight into the interaction mechanisms and as long as a linear relation between  $\ln k'_0$  and  $1/T$  exists, the definition of the activation parameters is valid. Despite the low activation energy of desorption,  $k'_0$  is the smallest for system IIIb. The entropy which in turn depends on the structure of adsorbed molecule and of the surfaces on which the adsorption or desorption process occur will also determine the rate of adsorption or desorption. The larger (more positive) the entropy of activation, the larger the reaction rate. Analysis of  $k_0$  or  $k'_0$  with respect to the activation parameters allows determination of the extent to which energetic or structural considerations determine the rates.

**Comparison of Thermodynamic Equilibrium and Activation Parameters for the Various Systems.** In the equilibrium studies of the sorption of pesticide on soil we may consider an adsorption and a desorption process taking place simultaneously at equilibrium:



where  $(\text{P})_e$  are the free pesticide molecules in the solution and  $(\text{P})_s$  are the adsorbed molecules. Their respective activities are  $a_e$  and  $a_s$ . The symbols  $k_f$  and  $k_b$  are the rate constants for the adsorption and desorption reactions, respectively. At steady state the following condition holds

$$a_e k_f = a_s k_b$$

or

$$a_s/a_e = k_f/k_b = K_0 \quad (6)$$

where  $K_0$  is defined as the thermodynamic distribution constant for the equilibrium adsorption process. For an equilibrium situation, the flow rate ( $F$ ) vanishes and hence the definitions of  $k_0$  and  $k'_0$  differ from that of the rate constants under no flow conditions. However, the de-

Table III. X-ray Diffraction Data before and after Desorption

| system <sup>a</sup>         | pH <sup>b</sup>  | $d_{001}$ , Å | $d_{001}$ , Å<br>(after water washed) | $d_{001}$ , Å<br>(after washing with CaCl <sub>2</sub> ) |
|-----------------------------|------------------|---------------|---------------------------------------|--|
| V clay                      | 5.7              | 9.7           | 9.7                                   | 14.3   |
| VI picloram and clay        | 3.2 <sup>c</sup> | 9.8           | 9.8                                   | 14.3   |
| VII picloram and clay (HCl) | 1.2 (HCl)        | 12.5          | 12.5                                  | 14.3   |
| VIII parathion and clay     | 5.7              | 15.8          | 15.8                                  | 15.8   |

<sup>a</sup> SPV Volclay bentonite (montmorillonite) from Wyoming (American Colloid Co., Chicago, IL). <sup>b</sup> pH of clay suspension. <sup>c</sup> Picloram solution has a pH 3.15.

ivation of  $k_0$  demonstrated that the ratio  $k_0/k_0'$  is equal to the ratio of the rate constants under no flow conditions. The distribution constant can be defined therefore by the ratio  $k_0/k_0'$  and the activation parameters can be related to the thermodynamic equilibrium parameters. In the derivation of  $k_0$  and  $k_0'$  it was assumed that activities are equivalent to concentrations. The ratio  $k_0/k_0'$  will therefore equal  $k_f/k_b$  only at low concentrations. This condition holds for all the data discussed below.

Values for  $K_0$  for picloram–Palouse system were determined previously (Biggar and Cheung, 1973). After correcting the appropriate units,  $K_0$  becomes 2.88, 2.28, and 1.80 mL/g while the ratio  $k_0/k_0'$  is 1.85, 1.41, and 0.97 for 15, 25, and 35 °C, respectively. From a simple mathematical derivation of the Van't Hoff equation (as represented in eq 7),  $\Delta H^\circ$  for the equilibrium reaction is the difference between  $\Delta H^\ddagger$  of the adsorption and  $\Delta H^\ddagger$ , of the desorption reactions:

$$\begin{aligned} -\frac{\Delta H^\circ}{R} &= \ln [K_{02}/K_{01}](1/T_2 - 1/T_1)^{-1} \\ &= \ln [(k_{02}/k_{02}')/(k_{01}/k_{01}')](1/T_2 - 1/T_1)^{-1} \\ &= [\ln (k_{02}/k_{01}) - \ln (k_{02}'/k_{01}')](1/T_2 - 1/T_1)^{-1} \end{aligned} \quad (7)$$

or

$$\Delta H^\circ = \Delta H^\ddagger - \Delta H^\ddagger \quad (8)$$

For system Ib, the value of the difference between  $\Delta H^\ddagger$  and  $\Delta H^\ddagger$ , for the kinetics of adsorption and desorption processes respectively is  $-5.9$  kcal/mol while  $\Delta H^\circ = -4.1$  as obtained from the equilibrium studies (Biggar and Cheung, 1973).

Results for the equilibrium adsorption of picloram by Palouse soil and of parathion by Panoche and Palouse soils were given previously (Biggar et al., 1978). At equilibrium, and at sufficiently low concentrations where the activity can be approximated by concentrations and the occupied fraction of the adsorbing surface is very small (the usual case for pesticides in the environment), the following should hold:

$$k_b C_s = k_f C_e (m/v) \quad (9)$$

or

$$\frac{k_f}{k_b} = \frac{k_0}{k_0'} = \frac{C_s}{C_e (m/v)} = \frac{x/m}{C_e} = K_{eq} \quad (9a)$$

where  $C_s$  is the amount adsorbed per unit volume of solvent,  $C_e$  is the equilibrium concentration of the solute,  $m/v$  is the weight of the adsorbent per unit volume of solvent, and  $x/m$  is the specific adsorption (amount adsorbed per unit weight of adsorbent). Equations 9 and 9a present another description of the system as compared with eq 5 and 6. For the conditions in which they apply, these two descriptions are equivalent as can be seen by comparing eq 9a and 6. While eq 5 and 6 represent a partition between two phases, bulk and surface, eq 9 and

9a represent an interaction between various species (solute molecules and adsorption sites) in the same phase.

At 25 °C,  $K_{eq}(k_0/k_0')$  for the systems picloram–Palouse, parathion–Panoche, and parathion–Palouse are 1.41, 4.45, and 45.9 mL/g, respectively. The ratio  $(x/m)/C_e$  for these systems is 1.06, 4.43, and 29.5 mL/g, respectively. The total concentration of the pesticide ( $C_s + C_e$ ) was in all cases 4  $\mu\text{g/mL}$ .

Considering the experimental uncertainties and the theoretical assumptions made both in the derivation of the rate constants  $k_0$  and  $k_0'$  and in the various equilibrium adsorption experiments, the agreement in the above comparisons is quite satisfactory. It indicates to a good approximation that adsorption in the systems studied may be viewed as a reaction in which a solute molecule collides with an adsorption site to form the adsorption complex. The term  $m/v$  represents the concentration of the free adsorption sites at sufficiently low concentrations. At higher concentrations  $m/v$  should be replaced by a different term. The desorption may be viewed as a "unimolecular" process by which the adsorption complex dissociates to a free site and a solute molecule. Interestingly, while the adsorption constants ( $k_0$ ) are relatively similar for the three systems, the desorption constants ( $k_0'$ ) vary by more than an order of magnitude. The large differences in the equilibrium adsorption arise mainly from the difference in the rate of desorption. If the pesticide is applied to the soil in one batch and then subjected to an occasional flow of water, the initial distribution of picloram and parathion in the systems studied may be rather similar but the subsequent downward mobility will be significantly greater with picloram in the Palouse soil. Parathion will move downward faster in Panoche than in Palouse soil and by inference it will move slower the higher the organic matter content.

Equations 9 and 9a are equivalent in their assumptions to the Langmuir isotherm at sufficiently low concentrations when the Langmuir isotherm is reduced to  $x/m = KC$ , that is, when only a very small fraction of the available adsorption sites are occupied. They also approach the Freundlich isotherm,  $x/m = KC^{1/n}$  as  $1/n$  approaches unity which is often the case (e.g., Biggar and Cheung, 1973). Equations 9 and 9a will hold true for most cases of pesticide residues in the environment.

**X-ray Diffraction Studies of Na-Saturated Montmorillonite.** The lattice spacings ( $d_{001}$ ) of the pesticide–montmorillonite samples before and after washing with distilled water and with 1.0 N CaCl<sub>2</sub>·2H<sub>2</sub>O are given in Table III. These spacings did not change after washing with distilled water for any of the four systems investigated. The  $d_{001}$  spacings conformed to the typical calcium-saturated montmorillonite spacing of 14 Å (Jackson, 1956) after washing with the CaCl<sub>2</sub> solution for systems V–VII (Table III).

As discussed previously, the presence of parathion in the interlayer spaces of sodium montmorillonite does not imply the same for the dominantly calcium montmorillonite in the Panoche soil under the conditions defined in the

present work. At any rate, for system VIII, the  $d_{001}$  spacing was not altered by washing, indicating the persistence of parathion inside the interlayer spacing. This may be due to the polar nature of the P-O and P-S groups which may strongly bond with the silicate sheets and the exchangeable cations. As expected,  $\text{CaCl}_2$  did not replace the nonionic parathion.

The resistance of parathion to desorption from the interlayer spacing sheds light on the long-term (15–16 year), low-level (0.06  $\mu\text{g/g}$ ) persistence of parathion in soil (Voerman and Besemer, 1970; Stewart et al., 1971). Parathion apparently is difficult to displace from the interlayer spacing by infiltration of water in the natural environment. Microbial degradation of parathion will be hindered in these interlayer areas (Hirakoso, 1969; Getzin and Rosefield, 1968; Lichtenstein et al., 1968). The common microorganisms in soil such as bacteria and Actinomycetes which have dimensions of 0.5–2  $\mu\text{m}$  are at least 300 times greater than the interlayer spacing. The parathion molecules are thus protected from microbial degradation but not against degradation by exoenzymes.

This report has examined the kinetics of desorption of picloram and parathion from Panoche clay and Palouse silt. The desorption kinetic reaction constants  $k_0'$  were calculated and their temperature dependence used to derive activation parameters. The merits of the thermodynamic interpretation of the behavior of pesticide in a complex system such as soil is stressed in view of the large variation in experimental conditions and methods of calculations usually employed. As conditions in soil are usually nonequilibrium and often dynamic, the separate study of the desorption and adsorption process is most useful.

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## Relation of Temperature to Ethylene Dibromide Desorption from Fumigated Wheat

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The desorption of ethylene dibromide from fumigated wheat aerated at temperatures of 0–45 °C as determined by extraction with two different solvents and by steam distillation was found to increase as the temperature decreased. The maximum amount of extractable residue was obtained with an acetone–water mixture while petroleum ether extracted only the less-tightly bound portion. Desorption of this portion seemed to be inversely related to temperature and the effect was found to be reversible. Labeled ethylene dibromide was used to substantiate the results found by chemical analysis and to determine residue rates of desorption at different relative humidities. Considerably greater desorption was found to occur at high rather than at low humidities.

Temperature has considerable influence on rate of diffusion of a fumigant into material during treatment and a corresponding effect on desorption afterward. Although more rapid diffusion and desorption might be expected as temperatures are increased, a study on halogenated fumigants by Biorai and Alumot (1975) showed faster desorption from cereal grains at low rather than at high temperatures. The authors implied that their observations seemed to disagree with expected behavior but their results gave clear indication that this situation did occur. Other work by Scudamore and Heuser (1973) and Jagielski et al.

(1978) had failed to show increased desorption at lower temperatures, and studies by Dumas and Bond (1975) on desorption of ethylene dibromide (EDBr) from apples showed reduction in desorption as the temperature was reduced.

To investigate reasons for variability in results and to establish the pattern of desorption of EDBr from wheat under laboratory conditions, residues remaining in wheat held at different temperatures and relative humidities (RH) for various time intervals were measured. Different methods of extraction were used to remove the residual fumigant and the extracts so obtained were analyzed by two GLC procedures; in addition, labeled EDBr-1,2- $^{14}\text{C}$  was used for residue analysis to allow comparative assessments of data from different methods.

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