

# Kinetics of Benalate Adsorption on Kaolinites

O. P. BANSAL\* and A. K. CHATURVEDI

Chemistry Department, D. S. College, Aligarh-202 001

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Kinetics of benalate adsorption of H-, Na- and Ca-saturated kaolinites have been investigated. The adsorption and desorption rate constants obtained were in agreement with those obtained from the Lindstrom *et al.* model, which proved useful in the simultaneous evaluation of adsorption and desorption rate constants. The activation energies, heats of activation and entropies of activation along with thermodynamic parameters were calculated. The rate constants and other parameters indicated a partly physical and a partly chemical adsorption of benalate on clay surface. Adsorption occurs by coordination and/or protonation of the exchangeable cations of the clay with amidic carbonyl group of herbicide and hydrogen bonding and dipole association at the crystal edge and basal surface.

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A knowledge of reaction kinetics at the solid-liquid interface is extremely important in understanding the adsorption-desorption process and its mechanism<sup>1,2</sup>. A number of researchers have studied kinetic reactions of pesticides adsorption-desorption using rate laws and reaction order<sup>3-5</sup>, but these models suffer from various limitations. Lindstrom *et al.*<sup>6</sup> for adsorption of organic molecules derived a rate expression which can be applied to the adsorption process, which is the net result of two opposing reactions, adsorption and desorption. Other workers have also successfully used this model to study kinetics of organic compounds on soils<sup>7</sup> and clays<sup>8,9</sup>.

The aim of present investigation was (i) to test the applicability of Lindstrom *et al.* equation for benalate (a herbicide)<sup>10</sup> adsorption to H-, Na- and Ca-saturated kaolinites and (ii) to compare the results of the Lindstrom's model with those obtained from the rate law expression, for the separate adsorption and desorption processes of benalate. From the rate constants, the thermodynamic functions of the adsorption processes have also been calculated.

## Results and Discussion

An examination of Table 1 shows that during benalate interaction with H-, Na- and Ca-saturated kaolinites, the model of Lindstrom *et al.* is satisfactory for evaluation of rate constants, as at the experimental temperatures (288–328 K) the values of rate constants derived from the rate law method were in good agreement with those calculated from the Lindstrom *et al.* model (within the experimental error range  $\pm 3-6\%$ ).

The adsorption rate constants  $k_1$  of benalate on H-, Na- and Ca-kaolinites at all experimental temperatures were greater than the desorption rate constant  $k_2$  (Table 1). The rate of adsorption and desorption increased with rise in temperature; the adsorption rate followed the order H-kaolinite > Na-kaolinite > Ca-kaolinite, while rate of desorption was in reverse order. The values of activation

energy  $E_a$ , which were lower for the adsorption processes than for desorption (Table 2) also suggests that adsorption of benalate is faster than desorption. The low values of  $E_a$  suggested that the process is partly physical and partly chemical. The values of activation energy also support the order of benalate adsorption on kaolinite.

TABLE 1—RATE CONSTANTS AS CALCULATED BY THE LINDSTROM *et al.* MODEL AND BY FIRST ORDER KINETIC RATE LAWS FOR THE ADSORPTION OF BENALATE ON H-, Na- AND Ca-KAOLINITES

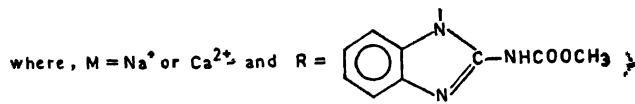
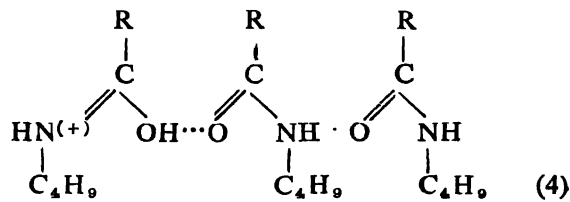
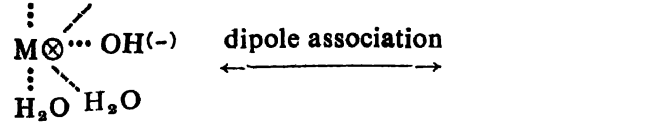
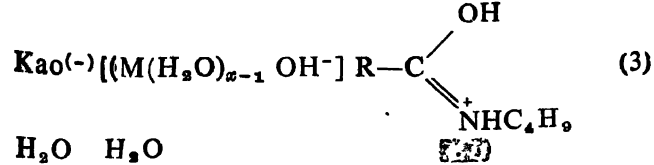
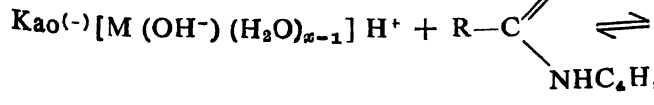
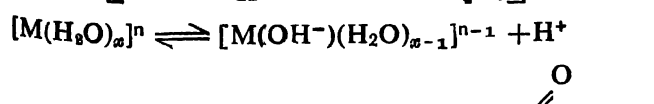
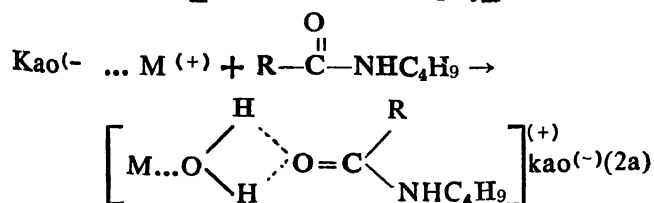
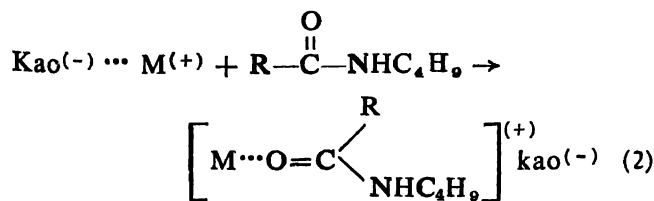
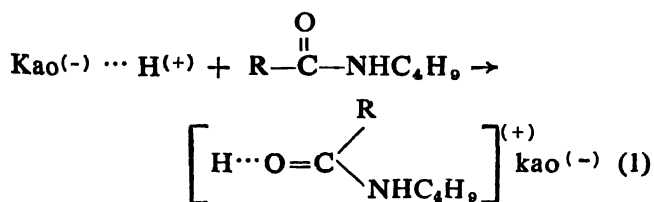
Clay	Temp. °C	Rate law method		Lindstrom <i>et al.</i> model	
		Adsorption $k_1 \text{ s}^{-1}$ $\times 10^{-5}$	Desorption $k_2 \text{ s}^{-1}$ $\times 10^{-6}$	Adsorption $k_1 \text{ s}^{-1}$ $\times 10^{-5}$	Desorption $k_2 \text{ s}^{-1}$ $\times 10^{-6}$
H-kaolinite	288	2.72	1.32	2.74	1.34
	298	3.96	2.53	4.06	2.50
	308	5.90	5.06	5.94	5.14
	318	8.48	10.86	8.54	10.80
	328	12.32	23.45	12.26	22.88
Na-kaolinite	288	1.70	1.24	1.74	1.26
	298	2.66	2.60	2.80	2.66
	308	4.00	5.56	4.10	5.48
	318	6.02	11.24	6.26	11.10
	328	9.10	22.00	9.50	21.80
Ca-kaolinite	288	1.26	1.40	1.30	1.44
	298	2.00	3.00	2.16	2.92
	308	3.36	5.70	3.40	5.58
	318	5.10	10.84	5.26	10.66
	328	8.72	23.00	8.84	22.66

The values of enthalpies of activation for the desorption process were higher than that for the adsorption process (Table 2), this is expected as the desorption process usually require more energy. The low values of the enthalpy of activation counter indicate chemisorption. So the adsorption of the benalate may be due to coordination and/or protonation<sup>12,13</sup>, hydrogen bonding and dipole association<sup>14</sup> on van der Waals forces. Metal ion bridged mechanism between the surface of clay and pesticide with or without water bridges<sup>15-17</sup> is as follows:

TABLE 2—KINETIC PARAMETERS FOR ADSORPTION AND DESORPTION PROCESSES\*

Temp. K	b	E <sub>a</sub> (kJ mol <sup>-1</sup> )		ΔH <sub>a</sub> (kJ mol <sup>-1</sup> )		ΔS <sub>a</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		ΔG <sub>a</sub> (kJ mol <sup>-1</sup> )	
		Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
H-kaolinite									
288	1.25							95.6	103.4
298	1.50							98.3	105.3
308	2.00	32.0±0.3	59.2±0.6	29.5±0.5	56.8±0.8	-230±0.8	-162.6±0.8	100.2	107.2
318	1.00							102.6	108.8
328	0.75							105.7	110.2
Na-kaolinite									
288	1.75							96.8	103.0
298	1.50							99.7	105.0
308	1.00	33.8±0.4	56.2±0.7	31.6±0.4	54.1±0.6	-227.1±0.5	-170.8±0.9	100.6	106.8
318	1.50							103.9	108.1
328	1.00							106.8	109.7
Ca-kaolinite									
288	1.25							87.7	102.5
298	1.75							100.2	102.5
308	1.25	37.0±0.5	52.7±1.1	35.0±0.5	50.7±1.0	-217.2±0.8	-180.6±0.9	103.6	106.5
318	1.00							104.6	107.8
328	0.75							107.2	109.1

\* Calculated from Lindstrom *et al.* model.



This proposition also finds support from IR and X-ray studies. Shifting of frequencies from 1660 to 1645 cm<sup>-1</sup> (C=O) and from 1680 to 1690 cm<sup>-1</sup> (C=N) during complexation of H-kaolinite suggests protonation of amide oxygen. Spectral shifts from 1660 to 1650 cm<sup>-1</sup> and 1680 to 1695 cm<sup>-1</sup> during Na- and Ca-kaolinite suggest coordination and/or protonation of pesticide molecule to Na<sup>+</sup> or Ca<sup>2+</sup> ion through the oxygen of amidic group with or without water bridges. X-Ray diffraction analyses indicate basal expansion of 0.19, 0.21, 0.20 nm during interaction of benalate with kaolinites (H-, Na- and Ca-form) respectively confirming interlayer adsorption on kaolinites.

The values of entropies of activation for adsorption and desorption processes at all experimental temperature, are negative (Table 2). The negative values point to the formation of activated complexes by coordination or association of benalate and exchangeable cations with resultant loss in the degree of freedom of benalate. Negative entropies of activation during the desorption processes were due to the benalate clay-complexes becoming activated before desorption<sup>11</sup>.

The values of the thermodynamic equilibrium constant K (Table 3) in all cases at experimental temperatures were more than unity and decreased

with increasing temperature, confirming that benalate had a higher preference for adsorption that decreased with the rise in temperature. The values also showed that the adsorption was in the order, H-kaol>Na-kaol>Ca-kaol. The values of  $\Delta G^\circ$  for studied interactions were negative and decreased with rise in temperature (Table 3). This indicated that the interactions at all the experimental temperatures were spontaneous with a higher preference for benalate on the clay surface. The magnitude of  $\Delta G^\circ$  values of the interactions showed that the interaction of benalate with the clay surface was an adsorption process<sup>17,18</sup>. The values of  $\Delta H^\circ$  indicated the exothermic nature of reaction, indicating that these processes are energetically stable and adsorption occurs through bonding mechanism<sup>19</sup>. The values of  $\Delta S^\circ$  indicated that adsorption complexes of benalate were stable. Association, fixation or immobilisation of the benalate molecules as a result of adsorption decreased the degree of freedom, which produced the negative entropy effects<sup>17</sup>.

The fraction adsorbed at any time ( $t$ ) was determined by the relation,

$$\phi(t) = \frac{C'_o - C(t)}{C'_o - C_\infty}$$

where  $C'_o = C_o V / (V_b + V)$  and  $\phi(t)$  was the fraction sorbed at time  $t$ ,  $C_o$  the initial concentration of benalate in the suspension at time  $t$ ,  $C_\infty$  the concentration of benalate in the suspension at equilibrium time,  $V$  the volume of adsorbate and  $V_b$  the volume of the buffer solution required to saturate the kaolinite surface.

For the desorption experiments, each of the H-, Na- and Ca-saturated clay suspensions (10 ml) was mixed with benalate solution (15 ml; 1500  $\mu\text{g ml}^{-1}$  in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ , 1:1). To the centrifugates of the complex formed, phosphate buffer of pH 7 (15 ml) was added and the volume was adjusted to 25 ml with distilled water. Five sets of experiments were performed at 15, 25, 35, 45 and  $55 \pm 0.1^\circ$ . The

TABLE 3—THERMODYNAMIC PARAMETERS FOR ADSORPTION OF BENALATE ON H-, Na- AND Ca-KAOLINITE

Parameter	H-kaolinite					Na-kaolinite					Ca-kaolinite				
	288	298	308	318	328	288	298	308	318	328	288	298	308	318	328
K	20.4	16.2	11.5	7.9	5.4	13.8	10.6	7.5	5.6	4.4	9.0	7.4	6.1	4.9	3.9
$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	-7.2	-6.9	-6.3	-5.5	-4.6	-6.3	-5.8	-5.2	-4.6	-4.0	-5.3	-5.0	-4.6	-4.2	-3.7
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	-26.1 $\pm$ 1.1					-23.2 $\pm$ 0.8					-21.0 $\pm$ 0.6				
$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	-66.1 $\pm$ 0.2					-58.7 $\pm$ 0.1					-53.3 $\pm$ 0.6				

( $\pm$ )=standard error of estimate.

### Experimental

The clay mineral used was kaolinite from American Petroleum Institute. A <2  $\mu\text{m}$  fraction was purified by sedimentation and centrifugation. The suspension was then converted into chloride free sodium and hydrogen ion saturated kaolinites by the reported method<sup>20</sup>. Calcium saturated kaolinite was prepared from the sodium form by ion-exchange technique. The clays were used immediately for the adsorption experiments. The base exchange capacity (BEC) of clay determined by the reported method<sup>21</sup> was 134  $\mu\text{eq per g}$  clay.

For the kinetic study, the clay surface was saturated with phosphate buffer of pH 7. Then samples (10 ml) of the appropriate kaolinite suspension were vigorously shaken in glass-stoppered tubes with standard benalate solution (15 ml; 1500  $\mu\text{g ml}^{-1}$  in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ , 1:1). Five sets of experiments at the temperatures 15, 25, 35, 45 and  $55 \pm 0.1^\circ$  were carried out in an air-thermostat. Preliminary kinetic measurements showed that the equilibrium was attained in 36 h. At 2 h intervals upto 48 h, samples were centrifuged and benalate estimated<sup>22</sup> in supernatant spectrophotometrically at 420 nm. The difference between the amount of benalate added and found in the supernatant after definite time intervals gave the amount of benalate adsorbed ( $\mu\text{m g}^{-1}$ ).

samples were shaken vigorously for 48 h. At 2 h intervals, samples were centrifuged and the amount of benalate estimated in the supernatant spectrophotometrically. All the experiments were conducted in triplicate with suitable blanks. The results are reproducible within  $\pm 3\%$  of experimental error.

The rate constants for adsorption ( $k_1$ ) and desorption ( $k_2$ ) were obtained from the equations,

$$k_1 \sum_1^N (X_1^{(1)})^2 + k_2 \sum_1^N X_1^{(1)} X_1^{(2)} = \sum_1^N X_1^{(1)} Y_1 \quad (1)$$

$$k_1 \sum_1^N X_1^{(1)} X_1^{(2)} + k_2 \sum_1^N (X_1^{(2)})^2 = \sum_1^N X_1^{(2)} Y_1 \quad (2)$$

where  $i$  is running index=1, 2, 3.....  $N$  and

$$Y_i = \phi(t_0 + i\Delta t) - \phi t_0 \quad (3)$$

$$X_i^{(1)} = \int_{t_0}^{t_0 + i\Delta t} (1-\phi) \left(1 - \frac{\phi}{2}\right) e^{-b\phi} dt \quad (4)$$

$$X_i^{(2)} = \int_{t_0}^{t_0 + i\Delta t} \left(1 - \frac{\phi}{2}\right) e^{b(2-\phi) - \frac{\phi}{2}} e^{b\phi} dt \quad (5)$$

where  $t$  is the length of each sub-interval  $= (t - t_0)/N$  and  $b = \alpha/RT$ , where  $\alpha$  is the energy stress constant for the sorbing surface.

By the process of least-square imbedding an acceptable region of  $b$  values was selected, starting with a least value of  $b$ . Thus, starting from  $b=0$  and for every increment of 0.25 values of  $Y_i, X_i^{(1)}$  were calculated for different experimental values of  $\phi$  from equations (3), (4) and (5). For evaluation of the intergral quantities trapezoidal rule was used. The process of increment of  $b$  values was continued till  $Y_i, X_i^{(1)}$  and  $X_i^{(2)}$  gave positive values of  $k_1$  and  $k_2$  from equations (1) and (2). From amongst the physically acceptable values of  $b$  thus obtained, a value of  $b$  was selected which gave the least value of  $E$  in the positive quadrant of the ( $E_0 = \min E$ )

$$\begin{pmatrix} b \geq 0 \\ k_1 k_2 \geq 0 \end{pmatrix}$$

the three-dimensional vector space ( $k_1, k_2, b$ ) of the equation,

$$E = \sum_{i=1}^N (Y_i - k_1 X_i^{(1)} - k_2 X_i^{(2)})^2 \quad (6)$$

from the estimated values of  $b$ , the required rate constants  $k_1$  and  $k_2$  were obtained.

A number of experiments showed that the adsorption and desorption of benalate on H-, Na- and Ca-kaolinites followed the first order kinetics as revealed by linear plots of  $\log(a-x)$  vs  $t$ . The rate constants were also calculated from the data of adsorption and desorption of benalate by kaolinite using the first order rate expression,

$$k' = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad (7)$$

where  $k'$  is the rate constant ( $k_1$  or  $k_2$ ),  $t$  the time (s),  $a$  the amount of benalate added and  $x$  the amount adsorbed or desorbed at time  $t$ .

Since temperature effect has been very useful in

providing an insight into the theory of all the rate processes, the energetics of adsorption of benalate on kaolinites were examined by temperature studies. The activation energy, free energy of activation, enthalpy of activation and entropy of activation were calculated with the help of rate constants using well-known equations<sup>11</sup>.

The equilibrium constant ( $k$ ) was obtained by the ratio ( $k_1/k_2$ )<sup>7</sup>, which enabled us to calculate the thermodynamic parameters for the physico-chemical equilibrium between benalate and kaolinites.

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