

HYDROLYSIS KINETICS OF ORGANIC CHEMICALS ON MONTMORILLONITE AND KAOLINITE SURFACES AS RELATED TO MOISTURE CONTENT

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Abstract—The effect of the surface acidity of montmorillonite and kaolinite on the hydrolysis rate constants of different agricultural chemicals was studied at variable moisture contents. Ethyl acetate, cyclohexene oxide, isopropyl bromide, 1-(4-methoxyphenyl)-2,3-epoxypropane, and N-methyl p-tolyl carbamate were chosen as representatives of classes of chemicals that exhibit acid-catalyzed, base-catalyzed, and neutral hydrolysis. In addition to being commercially available in pure forms, these chemicals have well-characterized homogeneous kinetics. The presence of montmorillonite or kaolinite in water suspensions had a small effect on the hydrolysis rate constants (k_h), whereas, the addition of moisture to oven-dried clays up to the limits of sorbed water resulted in an increase in the rate of hydrolysis of the epoxide by a factor of 10.

The increase in the hydrolysis rate constant suggests that the surface pH of montmorillonite or kaolinite might be 1–2 pH units lower than the bulk pH. The k_h value for the carbamate on Na-montmorillonite surface (bulk pH = 8.5) is 6.4×10^{-8} /sec which is equivalent to the rate constant at pH values ≤ 7 . The hydrolysis rate constant of the epoxide was reduced by a factor of 4 when the moisture content exceeded the limit of sorbed water. The addition of humic acid to the clay minerals resulted in about a 40% reduction of the epoxide hydrolysis rate constant.

Key Words—Humic acid, Hydrolysis kinetics, Kaolinite, Montmorillonite, Surface acidity, Water.

INTRODUCTION

The literature on the kinetic and thermodynamic effects of clay surfaces on organic chemicals is extensive, with the emphasis being on the unusually low pH detected at the surface of clay minerals. Using pH-sensitive indicators Mortland (1970), Bailey *et al.* (1973), Frenkel (1974), and Karickhoff and Bailey (1976) showed that surface pH is as much as 2–3 units lower than that of the bulk solution. Saltzman *et al.* (1974) found that the hydrolysis rate constant of parathion and methyl parathion on kaolinite increased by a factor of 100 when water was added up to the limit of sorbed water (11% wt/wt). A slight increase in the moisture content above that corresponding to sorbed water, however, resulted in a steep decrease in the hydrolysis rate constant. Using organic bases as indicators, Karickhoff and Bailey (1976) found that protonation of organic bases in a clay film exceeded that of the suspended clay system and increased as the moisture content decreased.

The experiments described in the present report were designed to evaluate this surface acidity effect on hydrolysis by using selected probe molecules that have well-characterized homogeneous kinetics in the absence of clays. The observed rate constants for hydrolysis in the presence of different clay minerals, either in suspension or as solids with variable amounts of moisture, were compared at or near the same bulk pH.

MATERIALS

Montmorillonite and kaolinite clay minerals from Ward's Natural Science Establishment, Rochester, New York, were fractionated by sedimentation. The $<2\text{-}\mu\text{m}$ size particles were found to contain small amounts of organic matter and carbonates. The samples were washed with sodium acetate solution (pH 5) and were treated with a few drops of H_2O_2 (Kunze, 1965). Ethyl acetate (EA), cyclohexene oxide (CHO), and isopropyl bromide (IPB) (from Mallinckrodt Company, Aldrich Chemical Company, and Metheson, Coleman and Bell Company, respectively) were found to be more than 98% pure by infrared and gas chromatography (GC) analyses and were used without additional purification. 1-(4-methoxyphenyl)-2,3-epoxypropane (EME) from the Aldrich Chemical Company was 99% pure by high performance liquid chromatography (HPLC) and was also used as received. N-methyl p-tolyl carbamate (MTC) was synthesized according to the procedure of Fujita *et al.* (1974). The water was deionized in a Milli-Q-Water purification unit and contained <0.1 ppm dissolved organic matter. Buffer solutions were prepared using 0.1 M potassium dihydrogen phosphate and 0.1 M NaOH according to the methods described in the CRC Handbook (West, 1975). Humic acid from Aldrich Chemical Company was suspended in deionized water (pH = 6) and stirred for 48 hr to remove soluble material.

Table 1. Hydrolysis rate constants in aqueous solution for EA, CHO, and IPB at 25°C.¹

Chemical	k_A (1/M·sec)	k_B (1/M·sec)	k_N (1/sec)
EA	$(1.14 \pm 0.15) \times 10^{-1}$	$(1.08 \pm 0.01) \times 10^{-1}$	$(5.90 \pm 0.01) \times 10^{-8}$
CHO	1.95 ± 0.00	$(0.301 \pm 0.148) \times 10^{-3}$	$(1.72 \pm 0.09) \times 10^{-6}$
IPB	²	²	$(4.08 \pm 0.70) \times 10^{-6}$

EA = ethyl acetate; CHO = cyclohexene oxide; IPB = isopropyl bromide.

¹ From Mill *et al.* (1981).

² Rate constants at pH values 3 to 11 are independent of pH, and the average observed value is 3.79×10^{-6} /sec (Mill *et al.*, 1981).

METHODS

Clay suspensions

All glassware, pipet tips, vials, and clay suspensions were autoclaved for 20-min periods at 115°C. The clay suspension was transferred to the vials in 1-ml aliquots. Aqueous solutions of EA, CHO, and IPB, were then added to the vials. The final concentrations were 10^{-4} M. Methyl ethyl ketone was used as an internal GC standard. The vials were placed in a constant temperature water bath at $25 \pm 0.1^\circ\text{C}$ on a shaker at a 45° angle for better mixing. For each treatment 20 time points were taken (one vial for each). For analysis, the vials were centrifuged at 10,000 rpm for 5 min at 4°C , and the supernatant liquid was then withdrawn. EA was analyzed by GC with a Poropak QS column at 150°C . CHO and IPB were analyzed on a Carbowax column at 106°C and 65°C , respectively.

Wetted clay

Montmorillonite and kaolinite samples were equilibrated with 0.01 M chloride salts of Na, Ca, or Mg to prepare homoionic clays. Oven-dried clay samples (24 hr heating at 105°C) were used for all experiments. By comparison of X-ray powder diffractograms of the oven-dried samples before and after rehydration and of samples dried over P_2O_5 , the heating was found to have no significant effect on the structures of the clay samples.

Humic acid (HA)-clay mixture was prepared by mixing the Na-clay with HA in the ratio of 2, 5, and 10 g of HA to 100 g of clay suspended in deionized water. The pH of the mixture was adjusted to 7.00 and the suspension was dehydrated. The HA-coated clay was used for the hydrolysis of epoxide as a 4% suspension in water, on HA-kaolinite with 5% H_2O , and on HA-montmorillonite with 30% H_2O .

Water was added to the clay samples according to the procedure described by Saltzman *et al.* (1976) to obtain the required moisture content. EME was introduced in an organic solvent (ether), and the solvent was removed by evacuation. Samples were placed in a constant temperature water bath at $25 \pm 0.1^\circ\text{C}$ on a shaker at 45° angle for better mixing. Two vials (0.1 g samples) were used for each time point taken. For analysis, the samples were extracted using 50% acetonitrile in water, equilibrated for 30 min, and centrifuged at

20,000 rpm at 4°C . The supernatant liquid was withdrawn and analyzed using HPLC on a C_{18} -Bondapack column with 50% acetonitrile in water at 2-ml/min flow rate, and a UV detector at 280 nm.

Concentrations of all starting materials and the products were evaluated by comparing their peak areas to those of a standard. In all experiments, the product balance was $100 \pm 3\%$. A similar HPLC method was used for analysis of MTC with 40% acetonitrile in water as the eluting phase with detection at 354 nm.

RESULTS

Hydrolysis of ethyl acetate, cyclohexene oxide and isopropyl bromide

Hydrolysis kinetic constants (k_h) for EA, CHO, and IPB were previously evaluated in water at 25°C over a wide range of pH values (Mill *et al.*, 1981, 1982). Table 1 summarizes the kinetic constants for each compound. At constant pH, the observed rate constant k_h follows a simple kinetic relation (Mabey and Mill, 1978):

$$\begin{aligned} d[C]/dt &= k_h[C] \\ &= (k_A[\text{H}_3\text{O}^+] + k_B[\text{HO}^-] + k_N)[C], \end{aligned} \quad (1)$$

where the observed rate constant for hydrolysis, k_h , is defined in terms of k_A , k_B , and k_N , which refer to acid-catalyzed, base-promoted, and water-promoted reactions, respectively. Solutions of 1×10^{-4} M EA, CHO, and IPB were heated at 25°C in the presence of 4.5% (wt/wt) of Na-, Mg- or Ca-montmorillonite, and the solutions were analyzed with time. Values of k_h at the measured bulk pH were estimated from regression of $\ln[C_t]$ vs. time following the usual first order relation

$$\ln([C_0]/[C_t]) = k_h t, \quad (2)$$

where C_0 and C_t are concentrations of the chemical at times zero and t . Calculated values of k_h at the same pH were estimated from the data in Table 1 and Eq. (1). Observed and measured values are compared in Table 2.

The hydrolysis constants for CHO and IPB are nearly identical with the constants for hydrolysis in homogeneous buffer solutions at the same pH. On the other hand, the hydrolysis rate constant for EA in the clay suspension is slightly higher than that in the buffer solution. The results suggest that the presence of the clay in a suspension form has a small effect on the

Table 2. Hydrolysis of EA, CHO, and IPB in a 4.5% (wt/wt) montmorillonite suspension at 25°C.¹

Cation	pH	Conc. (10 ⁴ M)	k _h (10 ⁷ /sec)	
			Calculated	Measured
EA				
Na	8.70	4.09	6.00	16.20 ± 0.065
Ca	8.12	6.63	2.01	8.91 ± 1.27
Mg	7.80	4.09	1.27	9.92 ± 1.64
Buffer ²	8.40	10.24	3.30	5.27 ± 0.86
CHO				
Na	7.30	6.60	17.7	8.60 ± 0.3
Buffer ³	7.30	6.60	17.7	8.7 ± 0.4
IPB				
Na	7.33	7.10	37.9	12.3 ± 0.7
Buffer ³	7.33	7.10	37.9	14.5 ± 3

¹ EA = ethyl acetate; CHO = cyclohexene oxide; IPB = isopropylbromide.

² Phosphate buffer, no clay.

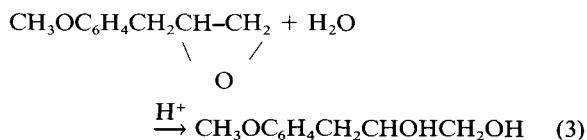
³ Borate buffer, no clay.

hydrolysis rate due to the limited interaction of the chemicals with the clay surface.

Because natural soils and clays are only partly hydrated, the effect of moisture content of clay on hydrolysis rates of two other less polar model compounds 1-(4-methoxyphenyl)-2,3-epoxypropane (EME) and N-methyl p-tolyl carbamate (MTC) were examined in detail. The hydrolysis rate of EME is constant at pH ≥ 7 and increases as the pH decreases. On the other hand, the hydrolysis rate of MTC is constant at pH ≤ 7 and increases with increasing the pH (Mabey and Mill, 1978). The hydrolysis rates of EME and MTC on low moisture clays should provide quantitative kinetic evidence for the presence of low pH surfaces on these clays.

Hydrolysis of 1-(4-methoxyphenyl)-2,3-epoxypropane

EME hydrolyzes to give the corresponding glycol via acid and neutral processes:



EME was chosen as a model epoxide for several reasons: (1) the epoxide is structurally similar enough to other aliphatic epoxides that its kinetic behavior on clay should provide some basis for generalizations about epoxide-clay interactions; (2) the aromatic structure is a convenient chromophore for HPLC analyses both for the epoxide and its hydrolysis product; (3) EME does not volatilize rapidly from the clay surface, and its solubility in water is extremely low; (4) the compound is commercially available in pure form at a moderate cost.

Hydrolysis rate constants for EME were measured

Table 3. Hydrolysis of 1-(4-methoxyphenyl)-2,3-epoxypropane on montmorillonite and kaolinite with bulk pH 7.

Moisture content (%) (wt/wt)	Conv. after 48 hr (%) ¹	10 ⁶ k _h /sec
Na-montmorillonite ²		
0	0	0
5	0	0
9	0	0
11	31	2.15 ± 0.22
19	47	3.74 ± 0.32
32	59	5.29 ± 0.60
50	50	4.06 ± 0.28
54	20	1.29 ± 0.13
Suspension ³	24	1.58 ± 0.16
Ca-montmorillonite ²		
0	0	0
4	0	0
5	45	3.46 ± 0.5
32	57	4.83 ± 0.24
50	47	4.73 ± 0.28
54	29	1.98 ± 0.20
Suspension ³	24	1.58 ± 0.16
Mg-montmorillonite ²		
0	0	0
4	0	0
5	47	3.67 ± 0.37
32	58	5.15 ± 0.50
50	30	2.06 ± 0.17
54	24	1.58 ± 0.21
Suspension ³	24	1.58 ± 0.16
Na-kaolinite ²		
0	0	0
1.3	0	0
2.5	35	2.50 ± 0.06
10.0	35	2.47 ± 0.10
12.5	20	1.29 ± 0.13
Suspension ³	21	1.36 ± 0.14

¹ All samples had better than 97% product balance, initial concentrations are 4–5 × 10⁻³ mmol/g.

² The clay samples are oven-dried to zero moisture after adjusting the suspension pH to 7.

³ The clay suspensions were made up of 5 g of clay in 100 ml water (bulk pH = 7.0).

in water, clay suspensions, and on clay surfaces with moisture contents ranging from 0 to 100% (on dry weight basis). The results given in Table 3 demonstrate the relationship between the amount of water associated with the clay surface and the hydrolysis rate constants. In all experiments the product balances between EME lost and glycol formed are >97%. The hydrolysis rate constant, k_h, of EME in water at pH 7 is 5.9 × 10⁻⁶/sec. The Na-montmorillonite suspension (1% wt/wt) with a bulk pH of 7 enhanced the hydrolysis rate by a factor of 2.7 (k_h = 1.58 × 10⁻⁶/sec). Similar results were obtained using Ca- and Mg-saturated montmorillonite (Table 3 and Figure 1).

Maximum hydrolysis rate constants were observed at moisture contents of 10–50% for Na-montmorillonite and 5–50% for Ca- or Mg-montmorillonite (Figure 1). An increase in the hydrolysis rate constant (k_h =

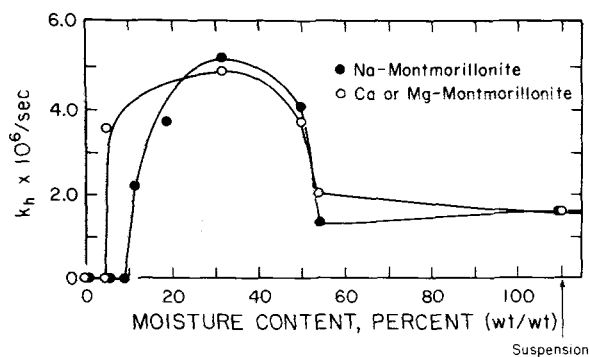


Figure 1. Rate of hydrolysis of 1-(4-methoxyphenyl)-2,3-epoxypropane on montmorillonite saturated with various cations.

$5.29 \times 10^{-6}/\text{sec}$) by a factor of 10 over the aqueous solution and a factor of 3 over the clay suspension was observed. It is apparent that the hydrolysis rate constant is greatly influenced by the presence of the clay, and it is related to the amount of water in association with the clay surface.

The Na-montmorillonite curve shows three different regions. Region I, where water is not available for hydrolysis ($k_h = 0$), has a moisture content of less than 10% (the equivalent value for Ca-, or Mg-saturated montmorillonite is 5%). Region II, where the catalytic effect of the clay surface is at a maximum, has a moisture content of 10–50% (5–50% for Ca- or Mg-saturated montmorillonite). Region III, where the clay surface has a limited effect on the hydrolysis rate, has moisture contents in excess of 50%.

The end of Region I corresponds with the saturation of the cations first hydration shell (approximately 10% for Na, and 5% for Ca- or Mg-montmorillonite). The end of Region III (50% moisture content) is the upper limit of bound water, because this moisture level was obtained by equilibrating the montmorillonite at 98% RH. A slight increase in moisture content (54% water) resulted in a steep decrease in the hydrolysis rate con-

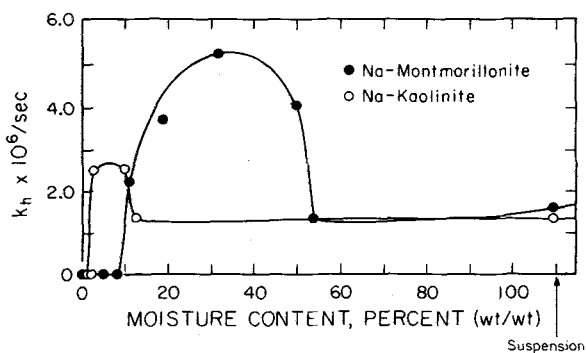


Figure 2. Rate of hydrolysis of 1-(4-methoxyphenyl)-2,3-epoxypropane on Na-saturated montmorillonite and kaolinite.

Table 4. Hydrolysis of 1-(4-methoxyphenyl)-2,3-epoxypropane (EME) on HA-coated Na-montmorillonite and Na-kaolinite.

Treatment	HA ¹ (%)	Initial EME (mmole/g)	Elapsed time (hr)	Conversion (%)	10 ⁶ k _h /sec
Na-montmorillonite	2	4.8	62	71	5.5 ± 0.17
30% moisture	5	4.6	62	61	4.3 ± 0.12
Content	10	4.5	62	53	3.5 ± 0.17
Na-montmorillonite	2	2.5	68	42	2.1 ± 0.27
4% suspension	5	2.5	68	43	2.2 ± 0.28
	10	2.5	68	39	1.9 ± 0.19
Na-kaolinite	2	4.4	65	39	2.0 ± 0.17
5% moisture	5	4.7	65	32	1.7 ± 0.16
Content	10	4.6	65	26	1.4 ± 0.17
Na-kaolinite	2	2.5	69	44	2.5 ± 0.15
4% suspension ²	5	2.5	69	46	2.4 ± 0.14
	10	2.5	69	41	2.0 ± 0.17

¹ HA = humic acid.

² 4% of clay-HA mixture.

stant. The presence of free water dramatically reduced the catalytic effect of the clay surface on EME hydrolysis rate by as much as 75%.

The hydrolysis of EME on the Na-saturated kaolinite with respect to moisture content is similar to that on Na-saturated montmorillonite; however, the maximum hydrolysis rate constant occurred at moisture contents of 2–10% (Figure 2). The results are in qualitative agreement with those obtained by Saltzman *et al.* (1976) using parathion and methylparathion with kaolinite; however, they noted as much as a 100-fold increase in rate in low water-content kaolinite. We found much less striking catalytic effects amounting only to a factor of 10 at most, possibly because phosphorus esters underwent surface-catalyzed hydrolysis involving selective bonding at surface sites.

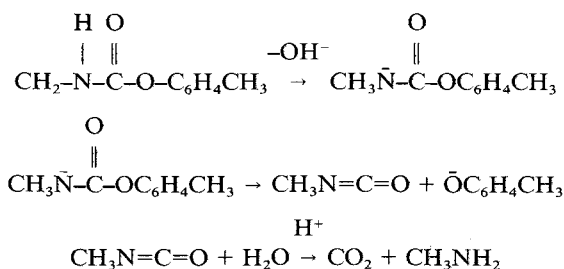
The effect of the presence of humic acid (HA) on the hydrolysis of EME was investigated, and the results are summarized in Table 4. The addition of HA to Na-saturated kaolinite and montmorillonite resulted in a reduction of the k_h values when the moisture content was in the sorbed water range (10–50%). Two percent HA on clay had the least effect due to the relatively small surface area which is coated by HA. In montmorillonite, 2% HA had no effect, whereas in kaolinite 2% HA resulted in a 20% reduction of the k_h value. Ten percent HA had the largest effect on both kaolinite and montmorillonite. The observed reduction in hydrolysis rate might be attributed to preferential adsorption on organic colloidal particles that might have been formed and by the different rate of hydrolysis on the surface of such particles as compared to the surface of clay particles. For HA-clay suspensions, the addition of HA resulted in a slight increase in the hydrolysis rate on both clays (Table 4).

Table 5. Hydrolysis of N-methyl p-tolyl carbamate (10^{-4} M).

pH	$10^8 k_h/\text{sec}$
0	7.5 ± 0.2
1	6.6 ± 0.4
3	6.0 ± 0.2
5	5.8 ± 0.3
7	6.7 ± 0.2
9	567 ± 17

Hydrolysis of N-methyl p-tolyl carbamate

The aromatic carbamate MTC hydrolyzes by base and neutral processes to give the phenol, amine, and CO_2 . A possible mechanism is given below:



The pH rate-profile for hydrolysis of MTC showed that MTC exhibits only water and base processes (Table 5). MTC should hydrolyze slower on clay surfaces because of the enhanced acidity (reduced basicity).

Na-montmorillonite (pH 8.5) and Na-kaolinite (pH 8.1) were used for the clay experiments. The rate of hydrolysis of MTC was measured on montmorillonite surfaces with 8 and 30% water and on kaolinite with 5% water (Table 6). As expected, rates of hydrolysis were slower on the clay than in solution. The k_h value for MTC on Na-montmorillonite surface (bulk pH = 8.5) is $6.4 \times 10^{-8}/\text{sec}$ which is equivalent to the rate constant at or below pH 7 (Table 5). Similar results were obtained with Na-kaolinite (Table 6). A reasonable explanation for the reduced rate of hydrolysis is that the H-ion concentration near the clay surface is higher than indicated by the bulk pH. If this explanation applies, and considering the hydrolysis rate constant of MTC, the pH on these clay surfaces could be as much as 2 pH units lower than the bulk pH. Thus, the estimated differences between the bulk pH and the surface pH for either EME or MTC are in good agreement. Table 6 also shows that with low water content (8%) no reaction occurs, as expected if all water is bound to the cations and is unavailable for reaction.

CONCLUSIONS

The results of the present study suggest that the catalytic effects of montmorillonite and kaolinite on the hydrolysis of EME and MTC are highly dependent on water content. At very low water content (<10% on

Table 6. Hydrolysis of N-methyl p-tolyl carbamate on Na-montmorillonite and Na-kaolinite.

Treatment	Initial EME (mmole/g)	Elapsed time (hr)	Conversion ² (%)	$10^8 k_h/\text{sec}$
Na-montmorillonite 8% H_2O Bulk pH = 8.2	4.60	168	0	0
Na-montmorillonite 30% H_2O Bulk pH = 8.5	3.47	192	4.4	6.50 ± 0.15
Na-kaolinite 5% H_2O Bulk pH = 8.1	3.29	240	3.9	4.67 ± 0.17

¹ EME = 1-(4-methoxyphenyl)-2,3-epoxypropane.

² Product balance > 97%.

montmorillonite), all water is bound tightly to cations and is unavailable for reaction (Bailey *et al.*, 1973). Because neither EME nor MTC were measurably sorbed to clay from water, it is unlikely that they are bound to active sites on the clay and react only when displaced by enough water.

Addition of more water in the range of sorbed (bound) water (up to 50%) enhanced the hydrolysis of EME and retarded the hydrolysis of MTC. A possible explanation to the reduction of the hydrolysis rate of MTC and the increase in rate of hydrolysis of EME is the lower pH at the clay surface. From the double layer theory the surface pH values on montmorillonite and kaolinite should be about 1.5–1.8 pH units lower than bulk pH (Stumm and Morgan, 1970). Water in excess of sorbed water reduces the catalytic activity of the surface by reducing the concentration gradient across the double layer thus providing a larger volume of free water in which reactions can take place at pH values closer to those in bulk water.

These results demonstrate that the moisture content of soil is an important parameter needed for judging the likely effect on hydrolysis reactions of agricultural chemicals in soil systems. The results further suggest that the surface effect is not restricted to special classes of chemicals but is a general phenomenon perhaps for all hydrolyzable structures which are catalyzed by H_3O^+ or HO^- .

The addition of humic acid to clay reduces hydrolysis rates by coating the surface and reducing the double-layer effect. Possibly, sorption of the organic molecule to HA also contributes to the reduced rates. This result suggests that in soils with moderate organic matter content, catalytic effects on hydrolysis will be smaller than in soils with low organic matter.

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REFERENCES

- Bailey, G. W., Brown, D. S., and Karickhoff, S. W. (1973) Competitive hydration of quinazoline at montmorillonite-water interfaces: *Science* **182**, 819.
- Frenkel, M. (1974) Surface acidity of montmorillonite: *Clays & Clay Minerals* **22**, 435-441.
- Fujita, T. and Kamashita, K. (1974) Physical-chemical parameters for structure-activity studies of substituted phenyl N-methyl carbamates: *Agr. Biol. Chem.* **38**, 1521-1528.
- Karickhoff, S. W. and Bailey, G. W. (1976) Protonation of organic bases in a clay-water system: *Clays & Clay Minerals* **24**, 170-176.
- Kunze, G. W. (1965) Pretreatment for mineralogical analysis: in *Methods of Soil Analysis*, C. A. Black, ed., American Society of Agronomy, Madison, Wisconsin, 568-577.
- Mabey, W. and Mill, T. (1978) Critical review of hydrolysis of organic compounds in water under environmental conditions: *J. Phys. Chem. Ref. Data* **27**, 383-915.
- Mill, T., Bawol, R., Partridge, I., and Mabey, W. (1981) Validation and Optimization of Hydrolysis Screening Test: Final Report, Battelle Columbus Laboratories, Contract T-6416(7197)-030, 86 pp.
- Mill, T., Mabey, W., Bomberger, D. C., Chou, T. W., Hendry, D. G., and Smith J. H. (1982) Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water: EPA Report, EPA-600/3-82-022, 329 pp.
- Mortland, M. M. (1970) Clay-organic complexes and interactions: *Adv. Agron.* **22**, 75-117.
- Saltzman, S., Yaron, B., and Mingelgrin, U. (1974) The surface-catalyzed hydrolysis of parathion on kaolinite: *Soil Sci. Soc. Amer. Proc.* **38**, 231-234.
- Saltzman, S., Mingelgrin, U., and Yaron, B. (1976) The role of water in the surface-catalyzed hydrolysis of phosphate esters on kaolinite: *J. Agric. Food Chem.* **34**, 739-742.
- Stumm, W. and Morgan J. (1981) *Aquatic Chemistry*: 2nd ed., Wiley Interscience, New York, 599-564.
- West, R. C., ed. (1975) *Handbook of Chemistry and Physics*: 55th ed., CRC Press, Boca Raton, Florida, p. D.

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Резюме—Исследовался эффект поверхностной кислотности монтмориллонита и каолинита на параметры скорости гидролиза различных сельскохозяйственных химических соединений при изменяющейся влажности. Были выбраны этилацетат, циклогексеновая окись, бромистый изопропил, 1-(4-метоксифенил)-2,3-эпоксипропан и N-метил р-талл карбамат, как характерные представители групп химических соединений, которые проявляют кислото-катализованный, основно-катализованный, и нейтральный гидролиз. Эти соединения, дополнительно к своей коммерческой доступности в чистом виде, имеют хорошо определенные однородные кинетики. Присутствие монтмориллонита или каолинита в водных суспензиях имело незначительный эффект на параметр скорости гидролиза (k_h), тогда как увеличение влажности в сухих глинах до максимальной величины адсорбции воды дало увеличение скорости гидролиза смеси в 10 раз.

Увеличение параметра скорости гидролиза указывает на то, что величина pH на поверхностях монтмориллонита или каолинита может быть на 1 до 2 pH меньше чем общая величина pH. Величина k_h для карбамата на поверхности Na-монтмориллонита (общая величина pH = 8,5) есть равна $6,4 \times 10^{-8}$ /сек, что является равнозначным параметру скорости при величинах pH ≤ 7 . Параметр скорости гидролиза смеси уменьшился в 4 раза, когда влажность превышала границу адсорбируемой воды. Результатом добавления гуминовой кислоты к глинистым минералам было уменьшение величины параметра скорости гидролиза смеси на порядок около 40%. [E.G.]

Resümee—Es wurde die Auswirkung der Oberflächenazidität von Montmorillonit und Kaolinit auf die Hydrolysegeschwindigkeitskonstante verschiedener im Ackerbau verwendeter Chemikalien bei verschiedenen Feuchtigkeitsgraden untersucht. Äthylacetat, Cyclohexenoxid, Isopropylbromid, 1-(4-Methoxyphenyl)-2,3-Epoxypropan und N-methyl-p-tolyl-Kabamat wurden als repräsentative Chemikalien ausgewählt, die Säure-katalysierte, Basenkatalysierte und neutrale Hydrolyse zeigen. Diese Chemikalien sind nicht nur in reiner Form käuflich erwerbbar, sondern haben außerdem eine gut untersuchte Homogenkinetik. Die Anwesenheit von Montmorillonit oder Kaolinit in Wassersuspensionen hat nur geringe Auswirkung auf die Hydrolysegeschwindigkeitskonstante (k_h), während die Zugabe von Feuchtigkeit zu im Ofen getrockneten Tonen bis zur Wassersättigung zu einer Zunahme der Hydrolysegeschwindigkeit von Epoxid bis zu einem Faktor 10 führt.

Die Zunahme der Hydrolysegeschwindigkeitskonstante deutet darauf hin, daß der Oberflächen-pH von Montmorillonit oder Kaolinit 1-2 pH-Einheiten kleiner sein könnte als der Gesamt-pH. Der k_h -Wert für Karbamat an Na-Montmorillonit (Gesamt-pH 8,5) beträgt $6,4 \times 10^{-8} \text{ sec}^{-1}$, was einer Geschwindigkeitskonstante bei pH-Werten ≤ 7 entspricht. Die Hydrolysegeschwindigkeitskonstante von Epoxid wurde um den Faktor 4 verkleinert, wenn der Feuchtigkeitsgehalt die Grenze des Adsorptionsvermögens für Wasser überschritten hat. Die Zugabe von Huminsäuren zu den Tonmineralen führte zu einer etwa 40%-igen Reduktion der Hydrolysegeschwindigkeitskonstante von Epoxid. [U.W.]

Résumé—On a étudié à de variables contenus d'humidité l'effet de l'acidité de surface de la montmorillonite et de la kaolinite sur les constantes d'allure d'hydrolyse de différents produits chimiques agricoles. On a choisi l'acétate éthyle, l'oxide cyclohexène, la bromide isopropyle, l'1-(4-méthoxyphényle)-

2,3-epoxypropane, et la carbamate N-méthyle p-tolyle carbamate comme représentants de classes de produits chimiques qui exhibent des hydrolyses catalysées par un acide, une base, et neutres. Ces produits chimiques sont disponibles commercialement, sous des formes pures, et ont en plus des cinétiques homogènes bien caractérisées. La présence de montmorillonite ou de kaolinite dans les suspensions aqueuses avait un effet moindre sur les constantes d'allure d'hydrolyse (k_h), tandis que l'addition d'humidité aux argiles séchées au four jusqu'à la limite de la sorption d'eau a résulté en une augmentation de l'allure d'hydrolyse de l'époxide par un facteur de 10.

L'augmentation de la constante de l'allure d'hydrolyse suggère que le pH de surface de la montmorillonite ou de la kaolinite pourrait être 1-2 unités de pH plus bas que le pH de masse. La valeur k_h pour la carbamate sur la surface montmorillonite-Na (pH de masse = 8,5) est $6,4 \times 10^{-8}/\text{sec}$ ce qui est équivalent à la constante d'allure pour les valeurs de $\text{pH} \leq 7$. La constante d'allure d'hydrolyse de l'époxide a été réduite par un facteur de 4 lorsque le contenu en humidité a excédé la limite de la sorption d'eau. L'addition d'acide humique aux minéraux argileux a résulté en une réduction d'à peu près 40% de la constante d'allure d'hydrolyse de l'époxide. [D.J.]