H-ION CATALYSIS BY CLAYS

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ABSTRACT

Acid clays prepared by electrodialysis or by treatement with dilute ($<$ about 0.1N) mineral acid solutions were largely Al-saturated, and had little catalytic effect on ester hydrolysis and sucrose inversion. On the other hand, clays exhaustively treated with cold 1N HCl were largely H-saturated, and served as effective H-ion catalysts. When various quantities of clay were used as catalysts, reaction rates were proportional to the concentration of H-ions in the system.

H-montmorillonites prepared from Plymouth, Utah bentonite and from Volclay bentonite were from 50 to 200 percent more effective catalysts for ethyl acetate hydrolysis than was HCl. For sucrose inversion, <2 μ H-clays had a somewhat greater catalytic effect than did HCl, while clay aggregates were much less effective catalysts. For ester hydrolysis, the degree of dispersion of the clay made little difference in its catalytic activity.

INTRODUCTION

That acid clays or soils catalyze such reactions as ester hydrolysis and sucrose inversion has been known for a long time. Wiegner (1931, p. 109) and Puri and Dua (1938, p. 121) reported quite extensive studies on H-ion catalysis by electrodialyzed clays and acid-treated soils, respectively. A common feature of their findings was that the catalytic efficiency of the clay or soil, measured by the ratio of the specific reaction rate to the total acidity of the catalyst, was much lower than that for soluble acids such as HCl.

Where ester hydrolysis is concerned, this is in marked contrast to the results of Davies and Thomas (1952, p. 1608) for catalysis by H-exchange resins. They found H-resins to be considerably more efficient catalysts than HCl, particularly for the hydrolysis of high molecular weight esters. Dodman and Kunin (1951, p. 1083) found H-resins to be less efficient than HCl in catalyzing sucrose inversion, but that the efficiency increased rapidly with both decreasing crosslinkage and decreasing particle size.

Since it is known that electrodialyzed or acid-treated clays are saturated partly with Al- rather than H-ions, it seemed desirable to investigate H-ion catalysis by clays of known H-saturation.

EXPERIMENTAL

Preparation and Characterization of Acid Clays

The clays used were: (1) water-stable aggregates (20-60 mesh) of Utah bentonite; (2) <2 μ Utah bentonite; (3) <2 μ Wyoming bentonite (Vol-

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clay); (4) unsorted Kamec halloysite from Spruce Pine, N.C.; and (5) montmorillonite from Little Rock, Arkansas.

The <2 μ montmorillonite had been freed of exchangeable bases by electrodialysis, and had aged for 1 year prior to use. The granular Utah bentonite and the halloysite were leached exhaustively with $N/20$ HCl and washed with distilled water.

It has been demonstrated previously (Coleman and Harward, 1953, p. 6045) that electrodialized or dilute mineral acid-treated montmorillonites and kaolins have both H and Al as exchangeable ions. Clays which have been aged in a base-unsaturated condition are often almost completely Al-saturated. Harward and Coleman (1954, p. 182) found that H-clays could be prepared by leaching montmorillonite with cold N HCl. In order to prepare H-clays, samples of granular Utah bentonite and halloysite were leached with 200 symmetry concentrations of N HCl, the time of contact being 20-30 minutes. After the acid treatment, the clays were washed by leaching with H_2O.

Samples of <2 μ Utah and Wyoming bentonites were H-saturated by similar treatment with cold N HCl. Suspensions of the electrodialized clays were made 1 N with respect to HCl. After standing for 15 minutes the supernatant was decanted and the flocculated clay was transferred to a large Buchner funnel and washed 3 times with small quantities of N HCl. The acid-treated clay was then transferred to a large beaker and stirred to effect dispersion in water. To remove excess HCl, as well as other free electrolyte, Amberlite MB-2, a mixture of H-cation and OH-anion exchangers, was added to the suspension. After 15 minutes of contact the clay was decanted through a 100 mesh screen. Batch treatment with MB-2 was repeated until a negative Cl test was obtained when a portion of the suspension was flocculated with $NaNO_3$ and $AgNO_3$ was added to the supernatant.

The Little Rock bentonite was treated with 1-10 HCl for 2 hours at 80° C. The hot acid-treated clay, which was in the form of water-stable aggregates, was washed on a filter until the wash water was Cl-free.

The nature of the acid clays was studied in the following ways: (1) Titration with NaOH in a salt-free system; (2) titration with NaOH in N KCl; (3) leaching with N KCl, followed by determination of H and Al in the leachate (titration of the leachate with NaOH, using methyl orange and phenolphthalein); (4) catalysis of ethyl acetate hydrolysis and sucrose inversion.

The acid characteristics of the clays are summarized in Table I. Cation exchange capacity refers to the me. of NaOH required to titrate 1 gm. (105° C) of clay to pH 8 in N KCl. Exchangeable H and Al, determined in the N KCl leachates, are also expressed as me. per gm. of dry clay.

The electrodialized and $N/20$ HCl-leached clays were almost completely Al-saturated. Treatment with a large excess of N HCl, however, yielded clay in which exchangeable H predominated. Except for the halloysite, all of the N HCl-treated clays were around 90 percent H-saturated.

The figures in the last column of Table I are the first order rate constants

Table I. — Properties of Acid Clays

Clay	Treatment	CEC[1] me. per gm.	Ex. H[2] me. per gm.	Ex. Al[2] me. per gm.	$10^5 k/N_{H+Al}$ for EtAc hydrolysis
Utah bent. $(2\,\mu)$	Electrodialysis	1.17	0.03	1.02	52
	N HCl	1.24	0.92	0.12	763
Utah bent. (gran.)	$N/20$ HCl	1.04	0.04	0.82	24
	N HCl	1.08	0.78	0.09	755
Wyo. bent. (2μ)	Electrodialysis	0.87	0.02	0.74	80
	N HCl	0.92	0.68	0.10	1084
Kamec halloysite	$N/20$ HCl	0.07	0	0.04	—
	N HCl	0.07	0.02	0.02	—
L.R. bent.	Hot 1-10 HCl	0.94	0.71	0.14	733

[1] CEC = me. NaOH to titrate 1 gm. (105° C) of clay to pH 8 in $1N$ KCl.
[2] Ex. H and Al are quantities of these ions replaced from 1 gm. (105° C) of clay upon leaching with $1N$ KCl.

for ethyl acetate hydrolysis at 25° C divided by the sum of exchangeable H and Al, and are measures of the catalytic efficiencies of the various clays. They will be discussed in detail later, but it is apparent that H-clays are much more effective catalysts for this reaction than are Al-clays.

Figure 1 shows the potentiometric titration curves of HCl-treated and electrodialized $<2\,\mu$ Utah bentonite in salt-free systems and in N KCl. The H-clays had strong acid type titration curves, as has been noted before (Coleman and Harward, 1953, p. 6045). Electrodialized clay in KCl had a titration curve similar to that of AlCl$_3$. The curves shown in Figure 1 are representative of those obtained with the other H- and Al-clays.

Catalysis by Acid Clays

In order to obtain satisfactory measures of ester hydrolysis or sucrose inversion in systems containing granular clays, shaking of the reacting mixtures was necessary. Because of this, the best temperature control available was to conduct the reactions in a room in which air temperature was maintained between 25° C and 26° C. A record of air temperature adjacent to the shaker was made with a hygrothermograph.

Systems containing definite amounts of HCl as catalyst were included in each run. When the reaction temperature for a particular run averaged near 25° C, k/N_H (the first order rate constant divided by the normality of the HCl catalyst) was close to the values reported by Harned and Pfansteil (1922, p. 2199) for ethyl acetate hydrolysis and for Leininger and Kilpatrick (1938, p. 2893) for sucrose inversion. On runs for which the average temperature was different from 25° C, all of the rate constants were multiplied by a factor which would convert the observed values of
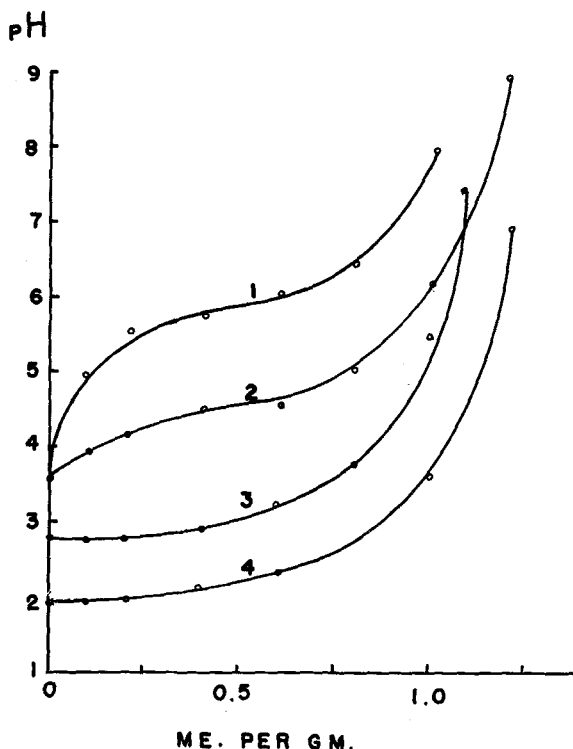
FIGURE 1. — Neutralization curves of < 2 μ Utah bentonite (1 per cent solids). (1) Electrodialyzed. (2) Electrodialyzed + N KCl. (3) N HCl-treated. (4) N HCl-treated − N KCl.

k/N_H for HCl to the accepted value at 25° C. This assumes the energy of activation for the clay-catalyzed reaction to be the same as for HCl.

The procedures for conducting the hydrolysis of ethyl acetate and the inversion of sucrose were similar. Into 125 ml. flasks were measured clay or HCl and sufficient water to give a final volume of 25 ml. The flasks were placed in the controlled temperature room several hours prior to the addition of ethyl acetate or sucrose. At the beginning of a run, 0.5 gm. of sucrose or 1 ml. of anhydrous ethyl acetate was added to each flask and shaking was begun. Reaction times for sucrose inversion varied from 1-6 hours, while ester hydrolysis was allowed to proceed for 12-24 hours.

At appropriate times, flasks were removed from the shaker and the contents were analyzed for reducing sugar by the method of Hassid (1937, p. 228) or for acetic acid by titration with NaOH. The clay did not interfere with the determination of reducing sugar. In measuring the quantity of acetic acid formed, the contents of each reaction flask was neutralized to phenolphthalein. Near the endpoint, KCl was added to afford more rapid neutralization of the clay. The acetic acid produced was taken as the

difference between titre and the amount of NaOH required to neutralize the catalyst.

Rate constants were calculated from the first order expression:

$$k = \frac{1}{t} \ln \frac{T_\infty}{T_\infty - T_t}$$

$t =$ time in minutes from the addition of sugar or ester until the reaction was stopped

$T_\infty =$ titre for complete inversion or hydrolysis

$T_t =$ titre at time t.

T_∞ was determined experimentally for each reaction by completely hydrolyzing 1 ml. of ethyl acetate and inverting 0.5 gm. of sucrose with HCl.

Ester Hydrolysis. — Some data for ethyl acetate hydrolysis have already been presented in Table I. H-clays were very good catalysts, Al-clays were not. Further information concerning the catalytic effect of exchangeable

TABLE II. — Hydrolysis of Ethyl Acetate by H-Clays and HCl

Catalyst	$10^2 N_H$	pH	$10^5 k$	$10^5 k/N_H$	$10^5 k/a_H$
HCl	—	—	—	634±12	—
H-Utah bent. (2 μ)	1.40	2.4	12.04	859	3010
	1.01	2.5	8.62	855	2690
	0.84	2.6	7.18	855	2970
	0.56	2.7	5.06	904	2530
	0.41	2.8	3.72	902	2320
	0.22	3.0	1.96	874	1960
	0.11	3.2	0.99	883	1570
				876±21	
H-Wyo. bent. (2 μ)	0.76	2.7	8.54	1120	4270
	0.61	2.7	7.13	1170	3560
	0.45	2.8	5.33	1180	3330
	0.30	3.0	3.54	1180	3540
	0.15	3.2	1.70	1130	2110
	0.08	3.4	1.03	1290	2570
				1180±59	
H-Utah bent. (gran.)	5.60	4.0	50.44	836	504000
	2.80	4.1	23.92	854	274000
	1.40	4.3	11.70	901	234000
				864±43	
H-L.R. bent. (gran.)	4.82	4.0	41.35	858	413000
H-Utah bent. (2 μ) +0.1N KCl	1.40	1.9	8.90	636	780
H-Wyo. bent. (2 μ) +0.1N KCl	0.76	2.2	4.89	643	725
H-Utah bent. (gran.) +0.1N KCl	2.80	1.7	20.24	723	973

H on ethyl acetate hydrolysis is given in Table II. The quantity of exchangeable H, expressed as the normality of H in the reaction mixture, was measured for each batch of clay immediately after the run in which it was used as a catalyst. This was necessary because H-clays change spontaneously into Al-clays when stored moist. Exchangeable H refers to that H which was replaced by leaching the clay with a neutral salt solution.

For each clay, the rate constant for ethyl acetate hydrolysis divided by the normality of H was approximately constant. Dispersed and granular Utah bentonite were equally effective catalysts, showing that the dispersion of the catalyst has little effect on ethyl acetate hydrolysis. The Wyoming bentonite was a more effective catalyst than the other clays, while the hot 1-10 HCl-treated Little Rock bentonite had about the same efficiency as Utah bentonite.

Of particular interest is the fact that the catalytic efficiencies of the clays were greater than that of HCl. From this one would infer that so far as promoting ester hydrolysis is concerned, the activity coefficient of exchangeable H-ions is greater than unity. This was also found by Davies and Thomas (1952, p. 1607) for H-resins. It must be emphasized that the values of k/N_H presented in Table II refer to the actual amount of exchangeable H, and not to the total acidity of the sample. Table I shows that exchangeable Al, though included in any measure of the total acidity of the clay, is not an effective catalyst for ethyl acetate hydrolysis.

Since the H-clays were more efficient catalysts than HCl, some runs were made in which the distribution of H-ions in the clay suspensions was changed by the addition of $N/10$ KCl. Table II shows that the addition of salt has resulted in values of k/N_H for the clays which closely approach the value for HCl.

The last column of Table 2 lists values for the specific rate constant divided by the H-ion activity of the various clay systems as deduced from potentiometric pH's measured with glass and saturated calomel electrodes. For the salt-free systems, k/a_H was much larger for the clays than for HCl, absurdly so for the granular clays. Except for the systems of high electrolyte content, potentiometric pH gave no indication of catalytic activity.

Davies and Thomas (1952, p. 1608) suggested that H-exchange resins are more effective than HCl as catalysts for ester hydrolysis in aqueous media because the ester is concentrated in the resin graules. Their explanation is compatible with the results of this work. Semiquantitative experiments showed positive adsorption of ethyl acetate from aqueous solution by granular Utah bentonite.

Sucrose Inversion. — Table III presents rates of sucrose inversion in the presence of acid clay and HCl. For the dispersed clays, k/N_H was somewhat larger than for HCl. However, the difference between the catalytic activity of the clays and HCl was not so large as in the case of ethyl acetate hydrolysis. Per unit concentration of H-ions, montmorillonite and halloysite were equally effective catalysts. As for ethyl acetate hydrolysis, the rate

Table III. — Inversion of Sucrose as Catalyzed by Clays and HCl

Catalyst	$10^3 N_H$	pH	$10^5 k$	$10^3 k/N_H$	$10^3 k/a_H$
HCl	—	—	—	6.7±0.2	—
H-Utah bent. (2 μ)	2.62	2.5	21.0	8.0	66.4
	2.10	2.6	16.1	7.7	64.1
	1.57	2.7	11.9	7.6	59.3
	1.05	3.1	7.4	7.0	93.2
	0.52	3.5	3.8	7.4	119.4
	0.21	4.0	1.6	7.5	160.0
				7.5±0.4	
H-halloysite	0.43	2.9	3.2	7.5	29.1
	0.31	3.1	2.3	9.5	28.5
	0.20	3.4	1.7	7.1	41.5
	0.06	3.8	0.5	7.9	31.2
				7.8±0.5	
H-Utah bent. (gran.)	0.76	4.2	1.21	1.6	192.1
	0.37	4.3	0.57	1.6	114.0
Electrodialized					
Utah bent. (2 μ)	1.7[1]	3.7	0.14	—	7.0
Al-Utah bent. (gran.)	3.4[1]	4.2	0.09	—	14.3

[1] Total acid normality, including exchangeable Al.

of sucrose inversion by a particular clay appeared to be proportional to H-ion concentration.

The granular Utah bentonite was not nearly as good a catalyst for sucrose inversion as dispersed clay or HCl. Dodman and Kunin (1951, p. 1083) attributed the similar behavior of H-exchange resins to restricted diffusion of sucrose within the exchanger particles. Since the dispersed clays were at least as effective catalysts as HCl in the present work, their explanation seems to apply here as well.

The Al-saturated clays were very ineffective catalysts for sucrose inversion. Per unit of exchange acidity, <2 μ H-Utah bentonite was around 100 times as active as electrodialyzed Utah clay.

As for ester hydrolysis, potentiometric H-ion activity was not a reflection of H-ion catalysis by the clays. It is interesting that k/a_H for electrodialyzed bentonite turned out to be very close to k/a_H for HCl. It may have been a fortuitous circumstance such as this which led Wiegner (1931, p. 109) to the erroneous conclusion that potentiometric pH and rate of sucrose inversion measure the same thing.

Since different concentrations of the same clay catalyzed sucrose inversion in proportion to the concentration of H-ions, it was of interest to study the rate of this reaction in the presence of partially neutralized clays. To this end, samples of <2 μ H-Utah bentonite were approximately half neutralized with hydroxides of Na, K, and Ca. Values of k/N_H for these

were 6.6, 7.5, and 7.5, respectively, as compared with 7.5 ± 0.4 for H-clay. Apparently the concentration of H-ions can be varied by changing base saturation without any large changes in catalytic efficiency.

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