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HEATING-OSCILLATING *X*-RAY DIFFRACTION STUDIES OF SOME ORGANO-MONTMORILLONITES

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Abstract

Organo-montmorillonites prepared by reacting amine salt ions and quaternary ions with sodium montmorillonite have been studied by the heating-oscillating *x*-ray diffraction technique. Correlation of the heating-oscillating *x*-ray diffraction data with thermogravimetric data shows that these organo-clays undergo a reorientation of the organic portion and then slowly decompose with increasing temperature. Fourier analysis indicates that the rearrangement is a shift from two peaks in the interlayer area to a single peak which results from a rotation of the aromatic portion of the organic ion from a vertical to a parallel orientation on the clay surface. The *x*-ray data combined with gas chromatographic analyses of the decomposition products indicates that a catalytic decomposition followed by a thermal desorption of the products is a possible explanation. Further, the apparent enhanced attraction of the organic material for the clay surface is postulated to be a result of strong attractive forces directed toward the active catalytic sites.

Introduction

The study of organo-montmorillonites has been of interest in recent years. Much of the work has been directed toward determining the type and extent of any bonding between the hydrocarbon proton of the exchanged or adsorbed organic material and the oxygen surfaces of the clay. Bradley (1945) and MacEwan (1948) have proposed an augmented C-H—O interaction between the two. From entirely different experimental approaches, McAtee and Concilio (1959) and Hoffmann and Brindley (1960) have indicated support for this interaction. McAtee suggested the attraction from the results of a thermal decomposition of an organo-bentonite and Hoffmann and Brindley observed the same effects from sorption work using polar organic molecules.

Studies on several of these organo-clays using the heating-oscillating *x*-ray diffraction technique leads to a degree of insight into the problem. In this technique, developed by Weiss and Rowland (1955), the temperature of the sample is increased slowly while continuously oscillating the *x*-ray goniometer over the peak to be followed. Any transformations that occur, or any reaction or decomposition of the organo-clay can be related to the configuration of the organic portion between the layers, and the position of the organic ion should be related to the kind of bonding involved and to the strength of such bonds.

Experimental Procedure

A homoionic sodium montmorillonite with a cation exchange capacity of about 95 meq/100 g of clay was prepared by passing a one per cent dispersion of centrifuged Wyoming bentonite, obtained from the Baroid Division of the National Lead Company, Houston, Texas, through an ion exchange column at 70° C. packed with Dowex-50 cation exchange resin in the sodium form. The organo-clays were prepared according to the procedure of McAtee (1958).

The *x*-ray analysis consisted of a heating-oscillating pattern run from 30° C. to about 350° C. depending on the decomposition temperature of the particular organo-clay. These were supplemented by one dimensional Fourier analyses calculated from *x*-ray data taken at 30° C. and at higher temperatures whenever possible.[1] Thermogravimetric determinations were run to differentiate between an internal rearrangement of the organic ion between the clay surfaces and an actual decomposition as indicated by a change in the basal spacing or diffraction intensity or both. A sample of approximately 100 mg was heated from 30° to 300° C., and any change in weight was recorded on an automatic recording balance.

A check on the decomposition products was made using gas chromatography. For these determinations a sample was slowly decomposed and the products were collected in diisopropyl ether. This solution was then run on a Beckman Model GC-2 gas chromatograph at 1× attenuation and a column temperature of 70 or 100° C.

DATA AND RESULTS

Samples investigated were a series of amine salt derivatives containing in common the benzyl group. These ranged from benzyl-ammonium montmorillonite to trimethylbenzylammonium montmorillonite. β-phenylethylammonium montmorillonite shows the effect of removing the phenyl group one carbon farther from the nitrogen atom and dibenzylammonium montmorillonite illustrates the effect of two benzyl groups on the same nitrogen atom. Dicyclohexylammonium montmorillonite represents a saturated cyclic organo-clay.

A series of four samples were prepared for each organic ion by adding 85, 100, 120, and 200 meq of organic cation per 100 g of the sodium montmorillonite. Table 1 illustrates the actual amount of organic cation exchanged onto the clay calculated from loss on ignition data.

From data obtained by the heating-oscillating patterns and from one

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[1] Fourier curves were calculated from *x*-ray data consisting of at least five or more orders of the basal spacing. Some of the curves obtained from the *x*-ray data at high temperatures where the number of basal lines was small cannot be expected to show any detail with regard to the Fourier analyses. However, several specimens of each sample were *x*-rayed and Fourier curves calculated and compared. Because all of the curves for a given organo-clay resulted in similar curves with respect to the number of peaks in the interlayer region, it is believed that the interpretation is sound.

TABLE 1. *X*-RAY DIFFRACTION AND ORGANIC CATION SIZE DATA

Ion Added	meq/100 g added	meq/100 g found	$d_{(001)}$ in Å at 30° C.	$d_{(001)}-9.5$[1]	van der Waals Width of ion, Å[2]
Type 1:					
Benzylammonium	200	90	14.7	5.2	6.4v
	120	87	14.7	5.2	4.0p
	100	83	14.7	5.2	
	85	84	14.7	5.2	
Methylbenzylammonium	200	113	14.8	5.3	6.4v
	120	95	14.8	5.3	4.0p
	100	93	14.7	5.2	
	85	89	14.8	5.3	
Dimethylbenzylammonium	200	117	14.6	5.1	6.4v
	120	101	14.6	5.1	4.0p
	100	99	14.4	4.9	
	85	85	14.5	5.0	
β-phenylethylammonium	200	99	14.9	5.4	6.4v
	120	95	15.0	5.5	4.0p
	100	86	14.5	5.0	
	85	78	14.6	5.1	
Type 2:					
Trimethylbenzylammonium	200	103	14.8	5.3	6.4v
	120	100	14.7	5.2	4.0p
	100	98	14.8	5.3	
	85	83	14.7	5.2	
Dibenzylammonium	200	99	15.1	5.6	6.4v
	120	94	15.1	5.6	4.0p
	100	87	15.0	5.5	
	85	76	15.0	5.5	
Type 3:					
Dicyclohexylammonium	200	97	14.5	5.0	7.0v
	120	97	14.5	5.0	4.5p
	100	89	14.3	4.8	
	85	89	14.4	4.9	

[1] 9.5 = (001) pyrophyllite spacing.

[2] Widths and areas of the organic cations were calculated using van der Waals radii and molecular configurations obtained from Pauling (1948).

v = vertical to the clay surface.

p = parallel to the clay surface.

dimensional Fourier analyses of the x-ray data, these organo-montmorillonites can be grouped into three types.

Type 1	Benzylammonium montmorillonite Methylbenzylammonium montmorillonite Dimethylbenzylammonium montmorillonite β-phenylethylammonium montmorillonite
Type 2	Trimethylbenzylammonium montmorillonite Dibenzylammonium montmorillonite
Type 3	Dicyclohexylammonium montmorillonite

First order basal spacings in degrees 2θ plotted against temperature for all samples containing their greatest amount of organic cation are given in Fig. 1. The first four curves of Fig. 1 are for Type 1 organo-montmorillonites listed above. The basal spacing for these clays remains constant at a value of about 6°2θ or 14.7 Å to a temperature of about 75° C. and then gradually decreases (2θ value increases) to a value of 13.6 Å at a temperature of 250° C.

Type 2 organo-clays, curves 5 and 6 of Fig. 1, showed no change in basal spacing (14.7 Å) until a temperature of approximately 275° C. was reached. This temperature approached the pyrolysis temperature of the organic material.

Curve 7 of Fig. 1 is for dicyclohexylammonium montmorillonite, Type 3 above. The basal spacing changes from about 14.5 Å to 13.9 Å at a temperature of about 100° C. then remains constant at this spacing to a temperature of 275° C. whereupon it decreases rapidly.

One dimensional Fourier analyses of the basal reflections of all samples were calculated from x-ray data taken at 30° C. Fourier curves for samples containing their greatest amount of organic cation are shown in Fig. 2. All of the curves with the exception of 3 and 7 show two peaks in the interlayer region. Curve 3, the Fourier curve for dimethylbenzylammonium montmorillonite, shows only a slight indication of two peaks. Some of the other samples of this organo-clay containing different amounts of the organic cation showed the two peaks more pronounced. Type 3 organo-clay, dicyclohexylammonium montmorillonite, showed only one Fourier peak in the interlayer region for all samples investigated at 30° C. This is shown in curve 7 of Fig. 2.

Fourier analyses of Type 1 organo-montmorillonites at temperatures of 130° C. (illustrated by curve 1 of Fig. 3) indicated that the two Fourier peaks obtained at 30° C. have changed to a single peak at the higher temperature. The temperature of 130° C. is slightly above the point where the basal spacing of these organo-clays starts to decrease. Type 2 organo-montmorillonites (illustrated by curve 2, Fig. 3), on the other hand, continue to show two Fourier peaks in the interlayer region to temperatures

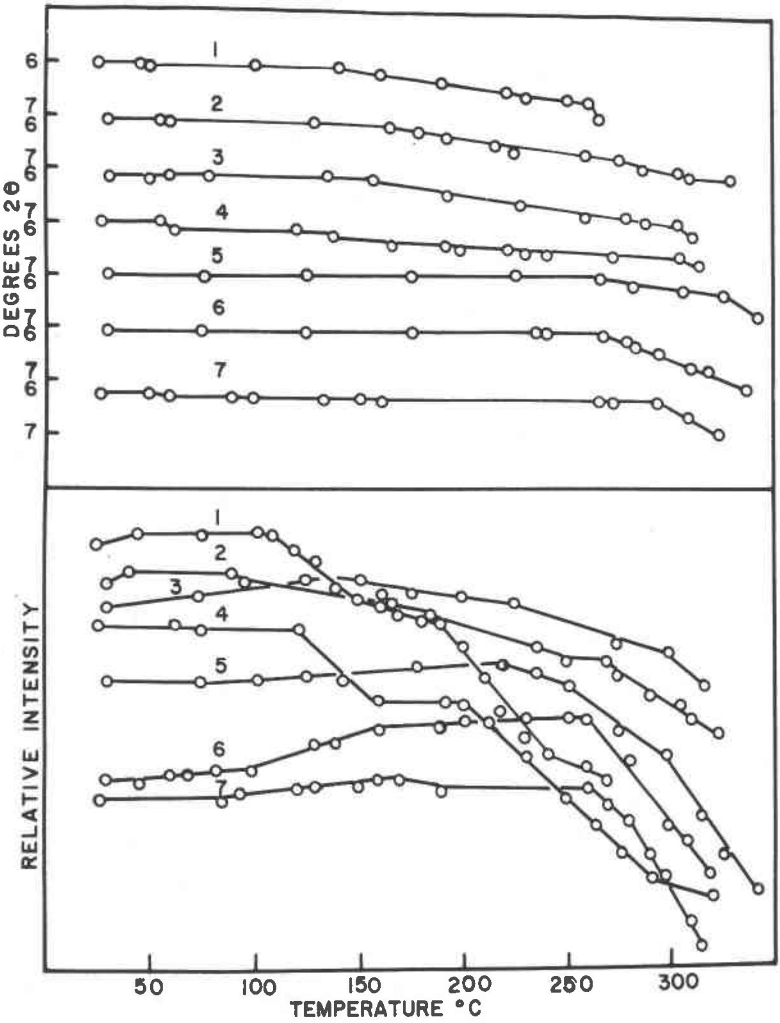

FIG. 1. Change in $d_{(001)}$ spacing in degrees 2θ and relative intensity of (001) peaks of organo-montmorillonites with increasing temperature (2.5° C./min). Each curve is a schematic representation of the heating-oscillating x-ray diffraction pattern.

1. Benzylammonium montmorillonite, 90 meq/100 g
2. Methylbenzylammonium montmorillonite, 113 meq/100 g
3. Dimethylbenzylammonium montmorillonite, 117 meq/100 g
4. β-phenylethylammonium montmorillonite, 99 meq/100 g
5. Trimethylbenzylammonium montmorillonite, 103 meq/100 g
6. Dibenzylammonium montmorillonite, 99 meq/100 g
7. Dicyclohexylammonium montmorillonite, 97 meq/100 g

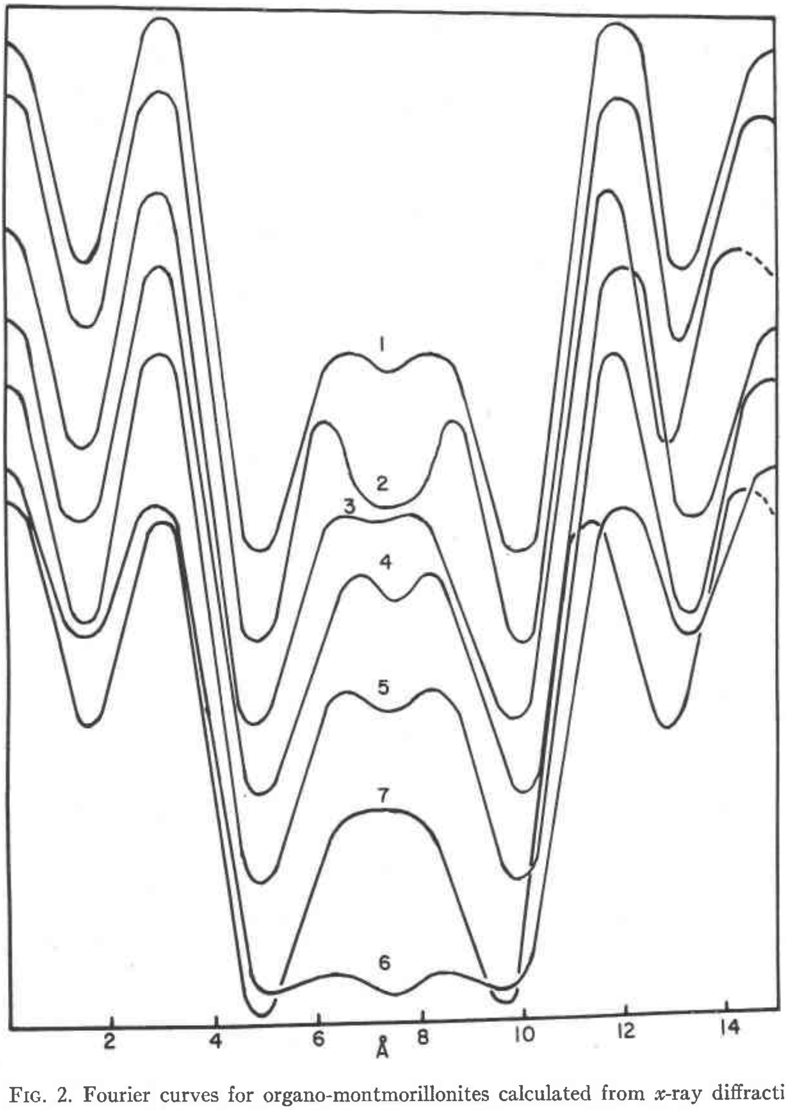

FIG. 2. Fourier curves for organo-montmorillonites calculated from x-ray diffraction data obtained at 30° C.

1. Benzylammonium montmorillonite, 90 meq/100 g
2. Methylbenzylammonium montmorillonite, 113 meq/100 g
3. Dimethylbenzylammonium montmorillonite, 117 meq/100 g
4. β-phenylethylammonium montmorillonite, 99 meq/100 g
5. Trimethylbenzylammonium montmorillonite, 103 meq/100 g
6. Dibenzylammonium montmorillonite, 99 meq/100 g
7. Dicyclohexylammonium montmorillonite, 97 meq/100 g

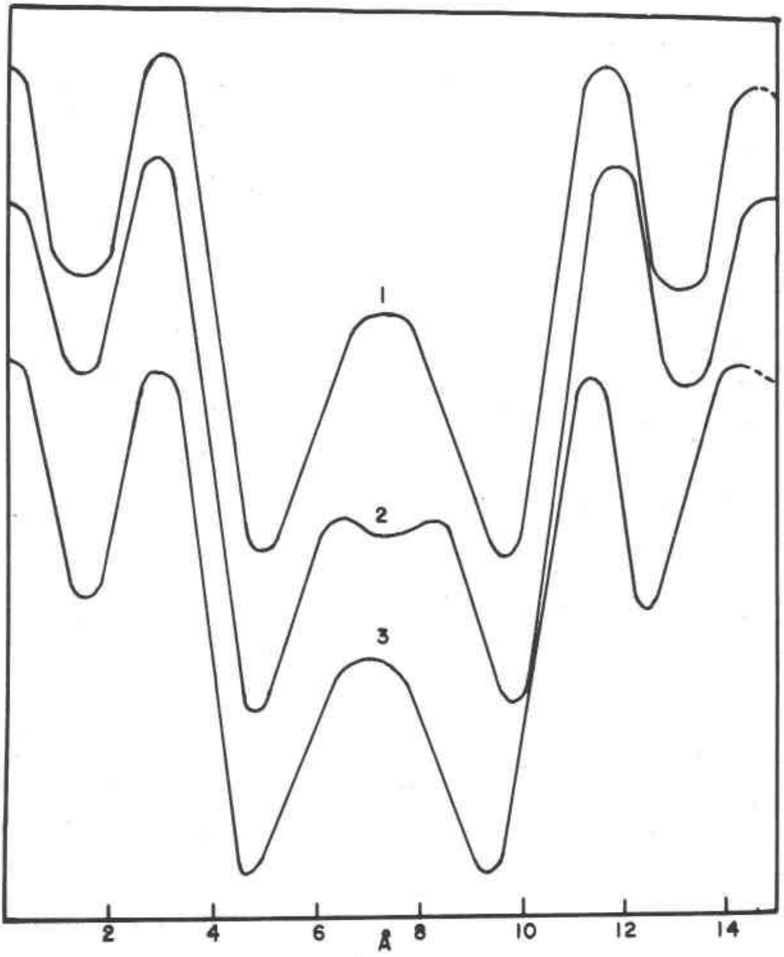

FIG. 3. Fourier curves for organo-montmorillonites calculated from x-ray diffraction data obtained at elevated temperatures.

1. Methylbenzylammonium montmorillonite at 130° C., 113 meq/100 g
2. Trimethylbenzylammonium montmorillonite at 200° C., 103 meq/100 g
3. Dicyclohexylammonium montmorillonite at 210° C., 97 meq/100 g

as high as 250° C. The decomposition point of these clays is shown in Fig. 1 to be about 275° C. Curve 3 of Fig. 3 shows that dicyclohexylammonium montmorillonite retains its single Fourier peak in the interlayer region to a temperature of 210° C.

Gas chromatographic analyses showed that toluene for the Type 1 samples and toluene and benzene for the Type 2 and 3 samples were obtained. Typical chromatographic curves for some of the samples are shown in Fig. 4.

Discussion of Results

The data obtained by three analytical techniques indicates that the organo-montmorillonites undergo a series of changes with increasing temperature which can provide information about the orientation of the organic ions and their bonding on the clay surface. Considering first the Type 1 organo-clays (benzylammonium montmorillonite, methylbenzylammonium montmorillonite, dimethylbenzylammonium montmorillonite and β-phenylethylammonium montmorillonite), x-ray diffraction data and Fourier analyses indicate that the organic ion is oriented with the aromatic portion in a vertical configuration on the clay surface at room tem-

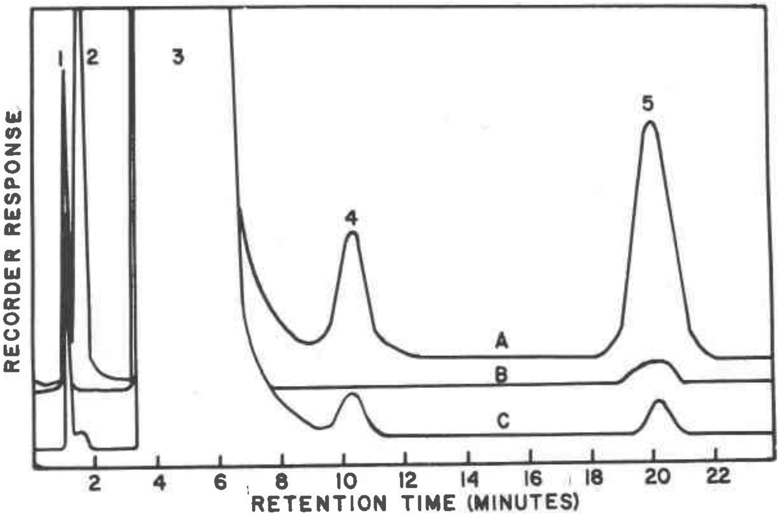

Fig. 4. Gas chromatographic traces.

Curve A: Decomposition products of dibenzylammonium montmorillonite in diisopropyl ether.

Curve B: Decomposition products of benzylammonium montmorillonite in diisopropyl ether.

Curve C: Trace amounts of toluene and benzene in diisopropyl ether.

Peak 1. Unknown material contained in the diisopropyl ether
2. Unknown material from the decomposition of dibenzylammonium montmorillonite
3. Diisopropyl ether
4. Benzene
5. Toluene

perature.[1] Further, the "d" values in Table 1 indicate that C-H—O contact distances are shortened in this configuration. The amount of shortening of the contact distance is about 0.5 to 1.0 Å. Dimethylbenzyl ammonium montmorillonite samples and lower meq samples of some of the other organo-clays gave results indicating that the aromatic group may be in some position intermediate between parallel and vertical arrangements. This is seen from the broad single peak indicated by the Fourier analyses.

This shortening is in agreement with the previous work of Bradley (1945) and MacEwan (1948) who first postulated the C-H—O interaction, and is also in agreement with the more recent work of McAtee and Concilio (1959) and the work of Hoffmann and Brindley (1960). The same type of shortened C-H—O contact is evident from the data of the Type 2 organomontmorillonites. Observed basal spacings are between parallel and vertical orientation values for the third Type, dicyclohexylammonium montmorillonite, and any shortening of the C-H—O contacts could not be detected.

Fourier analyses of Type 1 organo-montmorillonites show a change from two peaks to one peak in the interlayer area following the initial change in d-spacing. This alteration occurs at relatively low temperatures ranging from approximately 100° C. to 175° C. depending on the particular organo-clay and on the meq of organic cation on the clay. Thermogravimetric analyses show no loss in weight prior to this change in configuration, therefore the change is a true rearrangement of the organic portion of the organo-clay and decomposition of the organic ion, if any, cannot result in any lost products. The resultant organo-clay formed by this change in the orientation of the organic cation becomes rapidly disordered. As a consequence of this, it was not always possible to obtain oriented diffraction patterns at intermediate temperatures.

Amine salts decompose to give free amine by losing a proton at relatively low temperatures. It is reasonable to postulate, therefore, that the change in Type 1 organo-clays at low temperatures is a thermal decomposition of the amine salt ion to give free amine and hydrogen montmorillonite. These hydrogen clays are catalytically active and the free amine can then be catalytically decomposed and the resultant products thermally desorbed from the surfaces. This sequence is postulated by virtue of the loss in weight at temperatures greater than 175° C. ob-

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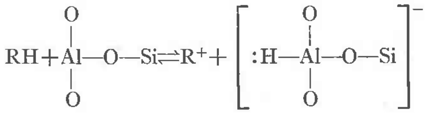
[1] Variations in the center to center distance of the two peaks of the organic cations are probably due to some ions leaning in less than a true vertical orientation. The *x*-ray data is not sufficient to clearly define the orientation other than to yield one peak or two peaks in the Fourier analysis.

served from thermogravimetric analyses and from gas chromatographic analyses of the decomposition products.

Trimethylbenzylammonium montmorillonite (Type 2) has enhanced thermal stability because of its molecular configuration, therefore, it would not be expected to lose a methyl group at low temperatures. The dibenzylammonium ion, because of its relatively large size (a projected area of about 90 Å^2 for the ions of Group 1) and because of the amount present, results in a crowding of the ions on the clay surface. This packing prevents the ions from rotating to a horizontal configuration, thus an enhanced thermal stability.

The dicyclohexylammonium montmorillonite behaves somewhat differently from the others. These samples show a region of stability, following a slight contraction in the basal spacing at 100 to 150° C., which is retained up to about 275° C. The chromatographic products observed from the decomposition were benzene and toluene. To obtain these products from dicyclohexylamine, a catalytic breaking of the amine as well as a breaking of one of the cyclohexyl rings must occur along with the dehydrogenation. Although the data from this work do not permit postulation of any catalytic mechanism for either cracking of the organic ions or for dehydrogenation of the dicyclohexylammonium ion, it lends itself to a comparison with previously postulated mechanisms for both phenomena.

Oblad, *et al.* (1951), discussed the chemical characteristics and structure of silica-alumina materials. These silica-alumina materials are effectively synthetically produced clays. These authors considered the active catalytic sites on the clay to be the tetrahedrally substituted aluminum ions in the silica layer. The hydrogen clay is the form that is catalytically active; however, these authors did not consider the acidity to be the factor influencing catalytic activity. Active centers arise due to the strained tetrahedrally coordinated aluminum ion shifting to the more normal octahedral coordination. Oblad *et al.* stated that this shift is induced by the silica and the surrounding substrate and represented it by the following reversible reaction:



$$\mathrm{RH} + \underset{\displaystyle \mathrm{O}}{\overset{\displaystyle \mathrm{O}}{\mathrm{Al}}}\!-\!\mathrm{O}\!-\!\mathrm{Si} \rightleftharpoons \mathrm{R}^{+} + \left[\, :\mathrm{H}\!-\!\underset{\displaystyle \mathrm{O}}{\overset{\displaystyle \mathrm{O}}{\mathrm{Al}}}\!-\!\mathrm{O}\!-\!\mathrm{Si} \,\right]^{-}$$

They then proposed that the cracking was a result of a betascission of the carbonium ion formed.

These authors have indicated that for a thermal cracking of alkylaryl hydrocarbons, the break is within the side chain, but for a catalytic cracking the break is next to the aromatic ring. An exception to this toluene which undergoes essentially no decomposition due to the difficulty in the formation of methyl carbonium ions.

Interpretating the data obtained from the organo-clays studied in this work in view of the above discussion, it seems evident that the changes occurring can be best explained by a catalytic mechanism. The enhanced attractions of the organic material for the clay surfaces is more logically the consequence of a strong attractive force such as would occur for a catalytic interaction. Although the C-H—O interaction proposed probably is present to some small extent, it cannot explain the strong forces that are indicated to occur at the clay surface. The shortened C-H—O distances found are probably due to an interpenetration of the protons into the oxygen cavities on the clay surface.

SUMMARY

A series of organo-montmorillonites was investigated using the heating-oscillating technique. In these clays the changes occurring between room temperature and 350° C. were considered. From *x*-ray diffraction, and thermogravimetric results and from gas chromatographic analyses of the decomposition products it was proposed that the organic ions undergo a catalytic decomposition followed by a thermal desorption from the clay surfaces.

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REFERENCES

BRADLEY, W. F. (1945) Molecular associations between montmorillonite and some polyfunctional organic liquids. *Jour. Am. Chem. Soc.* **67,** 975–981.

HOFFMANN, R. W. AND G. W. BRINDLEY (1960) Adsorption of non-aliphatic molecules from aqueous solutions on montmorillonite. *Geochim. Cosmochim. Acta,* **20,** 15–29.

MACEWAN, D. M. C. (1948) Complexes of clays with organic compounds. *Faraday Soc.* **44,** 349–367.

MCATEE, J. L. (1958) Random interstratification in organophilic bentonite. *Proc. 5th. Nat. Conf., Clays and Clay Minerals, Nat. Acad. Sci.-Nat. Res. Council, Publ.* **566,** 308–317.

——— AND C. B. CONCILIO (1959) Effect of heat on organo-montmorillonite complex. *Am. Mineral.* **44,** 1219–1229.

OBLAD, A. G., T. H. MILLIKEN, AND G. A. MILLS (1951) *Advances in Catalysis.* Academic Press, Inc., New York, **3,** 199–247.

PAULING, L. (1948) *The Nature of the Chemical Bond.* Cornell University Press, New York.

WEISS, E. J. AND R. A. ROWLAND (1956) Oscillating-heating *x*-ray diffractometer studies of clay mineral dehydroxylation. *Am. Mineral.* **41,** 117–127.

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