THE AMERICAN MINERALOGIST, VOL. 44, NOVEMBER-DECEMBER, 1959

EFFECT OF HEAT ON AN ORGANO-MONTMORILLONITE COMPLEX

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ABSTRACT

An organo-montmorillonite was heated under atmospheres of air, oxygen and nitrogen while following the changes in the basal spacing with a heating-oscillating x-ray diffractometer.

It has been shown that up to a temperature of about 180° C. a reversible expansion of the basal spacing takes place. With further heating this is followed by a very rapid collapse to a single organic layer between each two montmorillonite plates. Further heating reduces this to a system comprised of a monolayer of carbon between each two plates and then finally to a decrease in spacing to 9.8 Å, a fully collapsed montmorillonite.

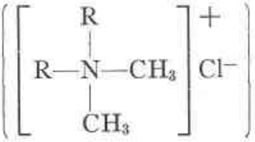
INTRODUCTION

The utilization of an oscillating-heating x-ray diffraction technique to study the clay minerals has been reported in several papers by Rowland, Weiss, and co-workers 1,2,3. Using the techniques described by these authors, oscillating-heating x-ray diffraction studies were made on an organo-montmorillonite complex formed by means of large organic cations. The decomposition of the organic portion of the organo-montmorillonite has been studied to gain knowledge with respect to the mechanism of interaction between the inorganic montmorillonite plates and the organic cation.

EXPERIMENTAL PROCEDURE AND RESULTS

The organo-montmorillonite used in these experiments was prepared from centrifuged Wyoming bentonite and dimethyldioctadecylammonium chloride. The bentonite was obtained from a deposit in the Mowry formation in the Colony, Wyoming area. Purification of the bentonite was accomplished by means of a Merco C-9 type centrifuge. The resulting bentonite slurry contained montmorillonite particles less than 0.8 micron in the largest dimension.

The organo-montmorillonite was prepared by adding dimethyldioctadecylammonium chloride



$$\left(\left[\begin{array}{c} R \\ | \\ R-N-CH_3 \\ | \\ CH_3 \end{array}\right]^{+} Cl^{-}\right)$$

to an aliquot of clay slurry, filtering, washing and drying. The sample was then ground and the exact amount of organic retained on the clay was determined by loss on ignition. The sample used in these experiments contained 115 *me* of organic/100 g. dry clay base.

The organo-montmorillonite sample was dispersed in methylethyl ketone and several drops of the dispersion were allowed to dry on a platinum—10% rhodium plate producing an oriented film of the organo-montmorillonite. The oriented sample was then placed in the furnace holder and a preliminary run made at room temperature to locate the positions of the diffraction maxima. The goniometer was then set to oscillate over the maxima to be scanned. The temperature of the furnace was then raised at a rate of approximately 5° C. per minute while oscillating and recording the diffraction maxima.

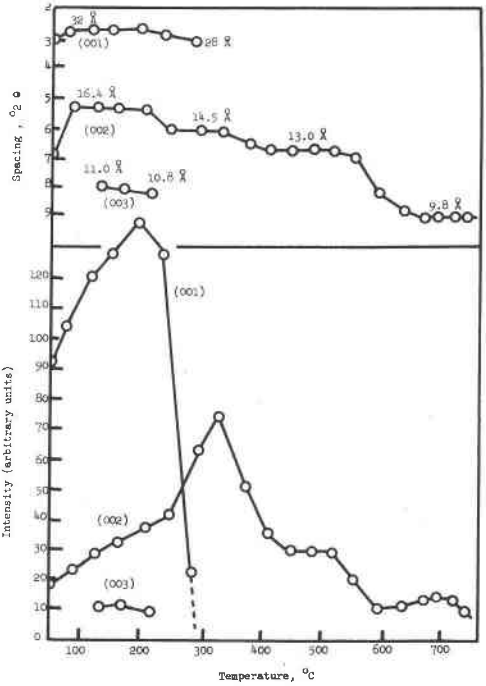


FIG. 1. Organo-bentonite, heated in air.

The graphs in Figs. 1 and 2 show changes in 2θ and intensity of the diffraction maxima of the organo-montmorillonite with increasing temperature. Figure 1 shows the data while oscillating over a wide enough region to follow the (001), (002) and (003) diffraction peaks and their changes. (The spectrometer trace is shown in Fig. 3.) The curves shown in Fig. 2 were produced while oscillating over a very narrow range of 2*θ* and manually changing the limits of oscillation so that the (001) diffraction maximum and its intensity could be accurately followed. The spectrometer trace for this experiment is shown in Fig. 4. The figures show that the (001) maximum drifts from 3.2° 2*θ* to 2.8° 2*θ* with increasing intensity up to a temperature of 75° C. It then stabilizes at 2.8° 2*θ* with continued increasing intensity up to a temperature of about 220° C. Then follows a very rapid decrease in intensity and a slight change in spacing to 3.2° 2*θ* up to a temperature of approximately 275° C., after which the diffraction maximum completely disappears.

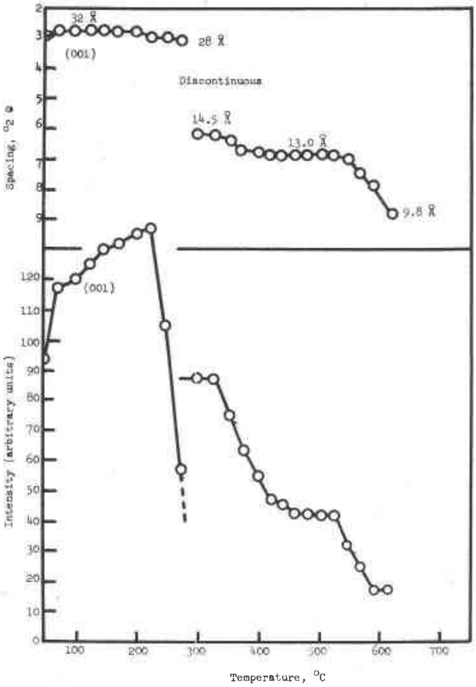


FIG. 2. Organo-bentonite, heated in air, oscillated over (001).

In Figs. 1 and 3 it is shown that the (002) diffraction maximum persists throughout the entire heating range of the experiment. This maximum at room temperature has a 2*θ* value of 7°. Heating causes the line to shift to 5.4° 2*θ* (75° C.) and remain there with a slight increase in intensity to a temperature of about 250° C. whereupon a very rapid increase in intensity takes place followed by a shift to 6.2° 2*θ*. The increase in intensity and spacing change occur simultaneously with the disappearance of the

(001) diffraction maximum. The intensity of the (002) line increases up to a temperature of 325° C.; it then decreases as the line shifts to 6.8° 2θ. Both the position and intensity of the line then remain constant to a temperature of about 525° C., after which the intensity decreases and the line shifts to 9.0° 2θ and remains constant to the end of the run.

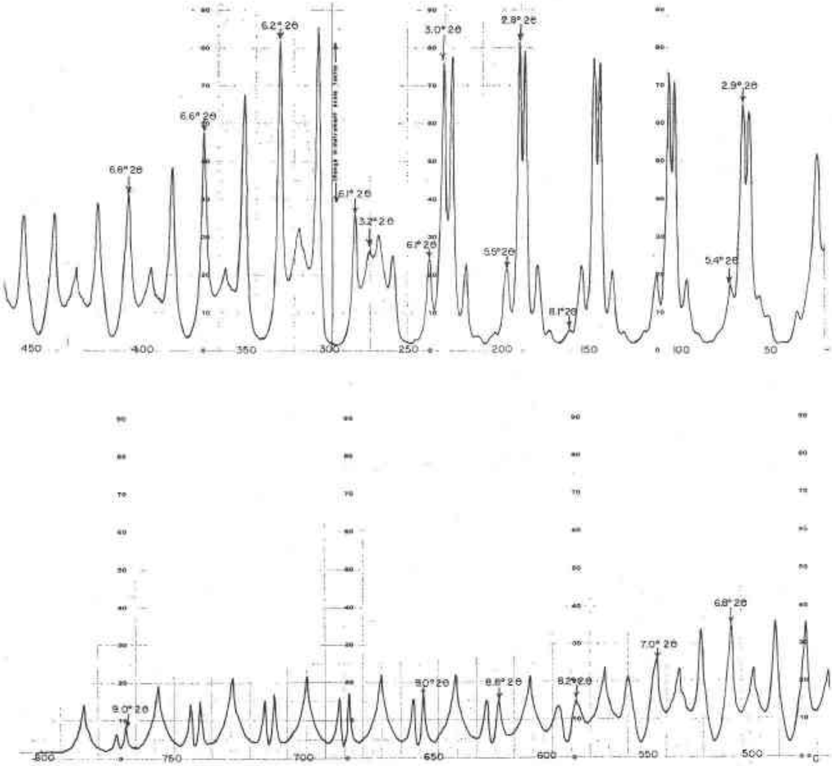


Fig. 3. Oscillating-heating X-ray diffraction diagram of (001), (002) and (003) for organo-bentonite heated in air from room temperature to 750° C.

The (003) line appears for only a short interval, approximately over the range of maximum intensity of the (001) maximum. The oscillation of the spectrometer was not over a wide enough range to determine the higher order spacings at temperatures above 250° C.

The curves shown in Fig. 2 and diffractometer trace in Fig. 4 demonstrate that the (001) diffraction maximum is discontinuous in the region of about 300° C. This demonstrates a rapid and complete change in the spacing between the montmorillonite sheets.

Separate portions of the organo-montmorillonite were heated in the x-ray oscillating furnace under oxygen and nitrogen atmospheres. This was accomplished by flowing the gas into the sample area at a rate sufficient to displace the air. The 2θ values and intensities for the several diffraction maxima for the sample heated in nitrogen and oxygen are shown in Figs. 5 and 6, respectively. The temperatures at which changes in the spacings occurred for the sample heated in oxygen are almost identical with those found when the sample was heated in air. The intensity curve of the (001) is also about the same, but the intensity of the (002) has a plateau from about 300° to 525° C. of fairly high intensity.

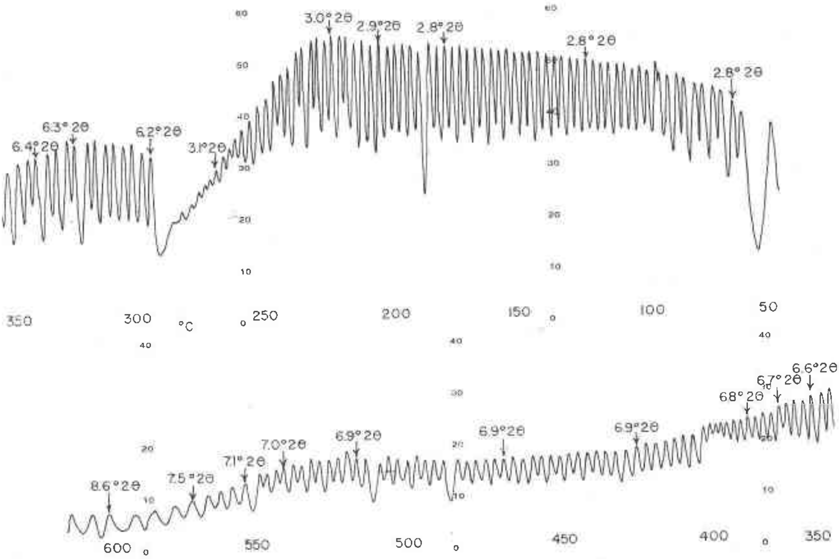


FIG. 4. Oscillating-heating X-ray diffraction diagram of (001) for organo-bentonite heated in air from room temperature to 625° C.

The 2θ and intensity curves for the sample heated under nitrogen (Fig. 6) are almost identical to the curves obtained when the sample was heated under air. About the only difference is a slight shift in the (002) from 6.8° 2θ to a value of 7.1° 2θ at a temperature of 450° C.

Curves showing the basal expansion and contraction of the organo-montmorillonite upon repeated heating and cooling are shown in Fig. 7. The oriented sample was heated from room temperature to a temperature of 170° C., the electricity turned off and the furnace allowed to cool to about 40° C. This was repeated several times, following the changes in position and intensity of the (001) and (002) diffraction peaks.

One dimensional Fourier synthesis curves for the organo-montmorillonite heated to various temperatures are shown in Figs. 8 and 9. To obtain the diffraction data needed for the Fourier synthesis, the sample was heated to the desired temperature and this temperature maintained while a complete diffractometer trace was obtained. From the position and intensity of the basal lines, the one dimensional Fourier curves were calculated. Fourier curves were obtained for diffractometer traces obtained at room temperature, 170, 280 and 425° C. These temperatures correspond to points of maximum intensity or plateaus found on the oscillating-heating diagram shown in Fig. 1. (The curves shown have not been normalized with respect to each other.)

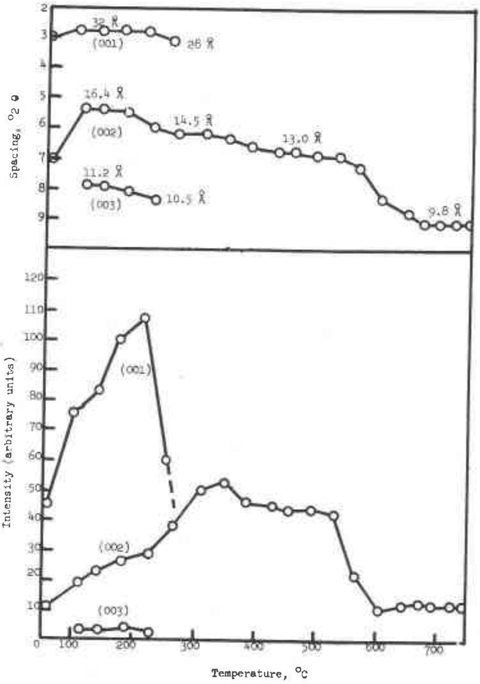


FIG. 5. Organo-bentonite, heated in O_2.

DISCUSSION

The general features of the oscillating-heating curves show that with slight heating the organo-montmorillonite undergoes a reversible type expansion from about 28 Å to 32 Å. Further heating causes a very sudden collapse of the expanded system from a four organo-layer system to a one layer system with a basal spacing of 14.5 Å. Additional heat causes the system to collapse slightly to 13.0 Å, then finally the lattice collapses completely to 9.8 Å.

The Fourier synthesis obtained for the organo-montmorillonite at room temperature shows a well established four-layer organo-montmorillonite (Figure 8A). The Fourier synthesis curves are "electron density" maps along the "*c*-axis" of the montmorillonite-organic complex. A maximum indicates a concentration of electrons and the distance between maxima is the distance from the center of a layer of atoms to the center of another layer of atoms. The distance from the center of the montmorillonite surface oxygen layer to the center of the first organic layer is about 3.9 Å, while the distance from the center of the first to the center of the second organic layer is 4.5 Å. These distances correspond very well with established data of Bradley (5) for his study of various organic materials associated with montmorillonite. The slight heating from room temperature to 170° C. causes a basal expansion to 32 Å. The corresponding Fourier synthesis is shown in Fig. 8B. Reference to Fig. 8

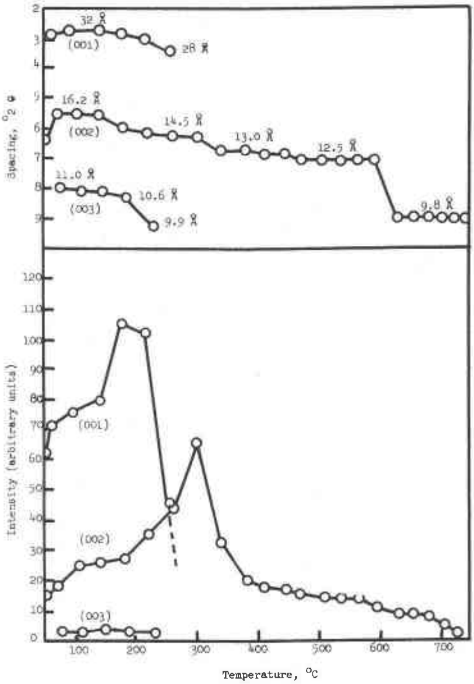


FIG. 6. Organo-bentonite, heated in N_2.

makes it apparent that the expansion takes place mainly between the two center organic layers. The negligible expansion of the layers associated with the montmorrillonite platelet surface shows that there is a high amount of energy of association and that the amount of heat added is not sufficient to cause many of the organic chains to become free. The expansion that is obtained (i.e., a change from 4.6 to 8.4 Å for the distance between the two central layers) along with the broadness of the second organic peak shows that some of the chains apparently become thermally active and cause the system to expand. Along with this expansion there is a very noticeable increase in the intensity of the (001) diffraction maximum. About 12% of this increase can be accounted for due to the increase in the Lorentz-Polarization factors with a decrease in 2θ. The total increase in the intensity of the (001) maximum is much greater than this as can be seen from Fig. 1. It is believed, therefore, that the system must be changing into a higher degree of order as the temperature is raised. The apparent change from "disorder" to "order" is reversible as shown in Fig. 7, therefore the higher order must be associated with the higher thermal energy of the organic chains at the elevated temperature. It is visualized that upon heating, some of the hydrocarbon chains begin to become thermally active and are able to move around to positions of greatest freedom. The heating, therefore, causes a certain amount of untangling of the hydrocarbon chains which in turn tends to cause a more uniform packing which gives rise to an increase in the intensity of the diffraction peak.

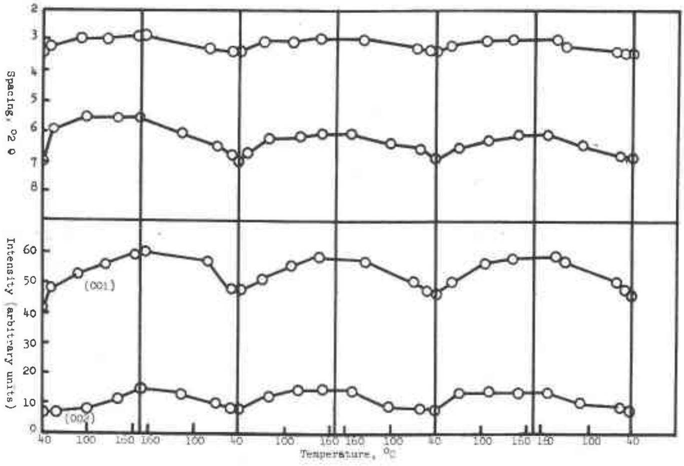


FIG. 7. Organo-bentonite, heated in air, sample repeatedly heated and cooled.

Following the initial expansion and upon heating the sample to a temperature of about 200° C., the hydrocarbon chains very suddenly start decomposing or desorbing so that the organo-montmorillonite loses the equivalent of two complete organic layers. In this region (shown as discontinuous in Fig. 2) there is an inefficiently *x*-ray scattering mixed layer assemblage collapsing to a single organic layer complex, which becomes apparent in the diffraction diagrams suddenly as its regularity improves. This type of collapse explains the changes in intensity of the (001) and (002) diffraction peaks shown in the various figures. The thermal decomposition or desorption leaves a residue consisting of a mixture of methylene groups, carbon and short chains on the nitrogen.

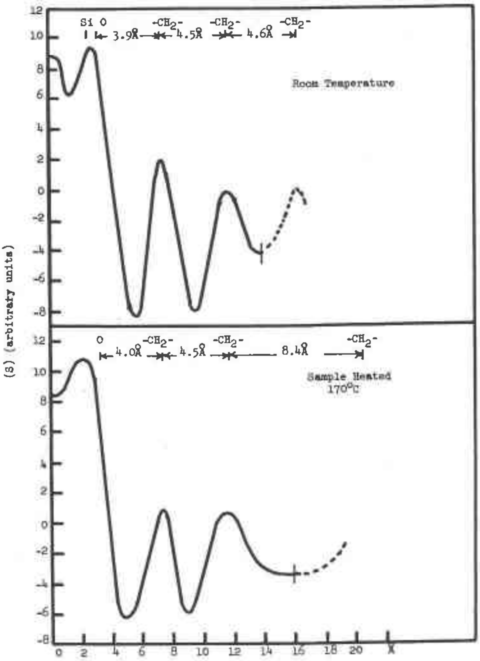


FIG. 8. Organo-bentonite, one dimensional Fourier synthesis.

In order to determine if this decomposition was strictly due to oxidation of the hydrocarbon chains, samples were *x*-rayed while heating and oscillating, while the sample area was flooded with oxygen and with nitrogen. Examination of the curves shown in Figs. 5 and 6 shows that an oxygen atmosphere does not cause the changes to take place at a lower temperature, nor does a nitrogen atmosphere allow the sample to be heated to a higher temperature before a collapse of the organo-clay takes place. This indicates that it is not oxidation of the chains that causes the sudden collapse, but a thermal rupture or pyrolysis of the bonds, or a thermal desorption of the molecule. Differential thermal curves shown by Jordan (4) indicate that above a temperature of 300° C. pyrolysis of the organic matter takes place for the larger organic cations.

The conclusions that can be drawn from the *x*-ray diffraction patterns and Fourier curves for the samples heated to 200–250° C. are that the interaction between the —CH_2— groups and the oxygen on the clay surfaces must be greater than simple Van der Waals forces and is probably an augmented attraction of the nature of a C-H—O bond as suggested by Bradley (5). At a temperature of about 225° C. there is enough heat available and the thermal activity is great enough so that the —CH_2— groups can break away from the surface oxygens and/or the methylene groups dehydrogenate allowing the system to contract to 14.5 Å.

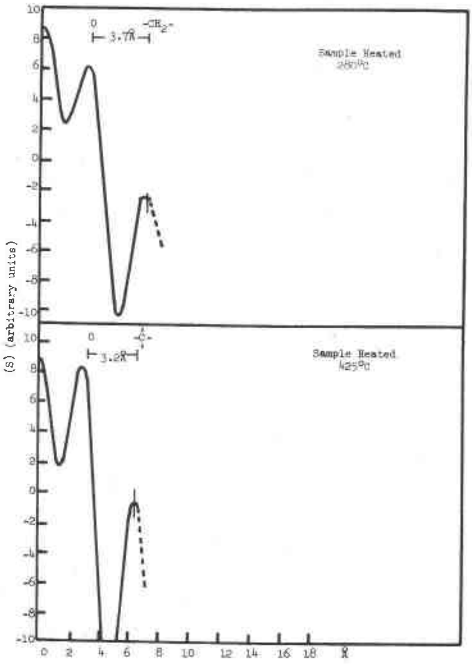


FIG. 9. Organo-bentonite, one dimensional Fourier synthesis.

Further heating of the sample, in air, oxygen or nitrogen causes a more complete decomposition of the hydrocarbon, probably leaving a residue of carbon and nitrogen. The presence of the carbon is quite apparent in that over the temperature range of 400° to about 550° C.; the sample is very black. The basal spacing during this period of heating is 13.0 Å which corresponds to the thickness of the montmorillonite plate, 9.6 Å, with a "graphite" layer of carbon, 3.4 Å. The c_0 distance reported for the hexagonal graphite is 6.707 Å (6), but this distance is for two complete basal layers of hexagonally associated carbon. Dividing 6.707 by 2 gives a value of 3.35 Å which is very close to the 3.4 Å distance found on heating the organo-montmorillonite to 400° C. This indicates, then, that a monolayer of carbon between each two montmorillonite plates is produced at this temperature.

At a temperature of about 500° C. the sample once more contracts, this time to a collapsed montmorillonite spacing of about 9.8 Å. The theoretical spacing for collapsed montmorillonite is 9.6 Å, therefore, with further heating of the organo-montmorillonite a slight reduction in the spacing may result. It is of interest to note that the final collapse of the organo-montmorillonite takes place at about the same temperature when the sample is heated in air, oxygen or nitrogen.

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Manuscript received March 23, 1959.