Journal of Thermal Analysis, Vol. 35 (1989) 1997–2008

THERMAL ANALYTIC STUDY OF THE ADSORPTION OF ACRIDINE ORANGE BY SMECTITE MINERALS

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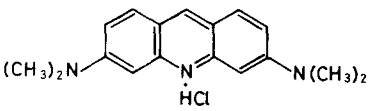
(Received December 14, 1988)

DTA, TG and DTG curves of montmorillonite and laponite treated with various amounts of acridine orange, were recorded in air, simultaneously with EGA curves of H_2O, CO_2, NO_2, CH_3 and C_2H_6. The thermal analysis curves could be divided into three regions representing dehydration of the clay, oxidation of the organic cation and dehydroxylation of the clay. The oxidation region showed two exothermic peaks representing the oxidation of H and C of the organic matter, respectively. Thermal analysis curves of laponite differred from those of montmorillonite. The profile of EGA curves of laponite did not change with the degree of saturation of the clay by the dye whereas those of montmorillonite were affected by the degree of saturation.

The adsorption of organic dyes by clay minerals has recently received increased attention in surface photochemistry [1–4]. Clay minerals may serve as supports of organic photochemical systems. They may organize the adsorbed molecules and thereby may direct energy transfer between molecules. In a study of the visible absorption spectrum of acridine-orange (AO, Scheme 1) adsorbed by montmorillonite, Cohen and Yariv [5] showed that this dye undergoes metachromasy, namely the absorption maximum of the $\pi \rightarrow \pi^*$ transition band shifts to shorter wavelengths. Metachromasy in aqueous solutions results from the association of



Acridine orange (AO)

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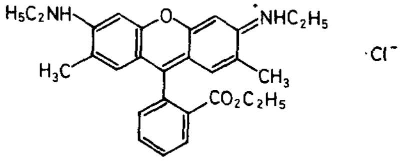
two dye cations and the blue shift is the consequence of π interactions between the aggregated cationic aromatic entities. Cohen and Yariv showed by X-ray study that up to a certain degree of saturation the *c*-spacing in the metachromic AO-montmorillonite complex was too small to account for the aggregation of AO cations in the interlayer space of the montmorillonite. They concluded that with a *c*-spacing of about 1.3 nm in AO-montmorillonite complex metachromasy resulted from π interactions between the oxygen plane of the montmorillonite and the aromatic dye. A *c*-spacing greater than 1.5 nm may be due to a bilayer or tilting of the cationic dye relative to the aluminosilicate layer. In the latter case it is possible that the interlayer space is populated by dimers of the cationic dye. Recently Grauer et al. [6] showed that π interactions are obtained between montmorillonite and cationic dyes, but not between laponite and the same cationic dyes. According to Yariv [7] the substitution of Si by Al is essential for π interactions between the oxygen plane and the aromatic entity. An oxygen atom of an Si–O–Al group is able to donate an electron pair to a π antibonding orbital of the cationic dye. Thus, this type of bonding may occur with montmorillonite but not with laponite. Recently it was shown that the cationic dye proflavine, which is of the same family as AO, does not form π interactions with the oxygen plane of laponite [8]. DTA has been widely used for the study of organo-clay complexes [9]. In the present communication we shall describe an improved thermal analysis method in which combustion products which are obtained during gradual heating, are mass-spectrometrically analyzed simultaneously with DTA and TG runs. This technique was previously described [10]. Thermal analysis curves of montmorillonite and laponite, both treated with AO, were recorded in order to determine whether the π interaction has any effect on the thermal behaviour of the organo-clay complex.

In a recent publication [11] we described the thermal analysis of montmorillonite and laponite treated with the cationic dye rhodamine 6G (R6G Scheme II). Due to steric hindrance the adsorption of rhodamine 6G by montmorillonite is not accompanied by π interactions between the oxygen plane and the aromatic entity. In the present communication we shall compare the thermal analysis curves of AO treated clays with those of the R6G treated clays.



Rhodamine 6 G (R6G)

Experimental

AO was supplied by BDH. Laponite XLG (a synthetic Na-hectorite) was kindly donated by Laporte Industries, Ltd., U.K. Montmorillonite (Wyoming bentonite) was supplied by Ward's Natural Science Establishment, Inc. Air-dried clay samples (250 mg) were dispersed in 20 ml of water. After an aging period of 24 hours, various amounts of the dye solution were added dropwise to the well-stirred clay suspension. The suspension was kept in the dark and after 24 hours the organo-clay was separated by centrifugation. Samples were washed three times with distilled water to remove excess dye.

Oriented samples of AO treated clay were prepared for X-ray diffraction by drying the suspension on glass slides. X-ray diffraction patterns were recorded on Philips PW 1730 diffractometer.

Thermoanalytical experiments were carried out under a flow of air on a Mettler TA-1 thermal analysis instrument coupled with a Balzers quadrupole mass-spectrometer [10]. Samples of 20 mg were used for each run. The rate of the air flow was 1.9 l.p.H. Heating rate was 10 deg/min. Calcined kaolinite was used as a reference material.

The following atomic masses were used for the gas evolution curves: H_2O, 18; CO_2, 44; NO_2, 46; CH_3, 15 and C_2H_6, 30.

Results and discussion

X-ray study

Oriented specimens of clay samples treated with various amounts of AO were examined by X-ray diffraction under ambient conditions (Table 1). Heating natural montmorillonite or laponite at 195° for six days results in a *c*-spacing of 1.0 nm due

Table 1 Basal spacings (in nm) of air-dried montmorillonite and laponite treated with different amounts of AO

mM AO per 100 g clay	Montmorillonite		Laponite
0	1.28		1.34
4	1.44		1.37
25	1.25		1.27
50	1.31	(1.27 sh, 1.52 sh)	1.39
75	—		1.38, 1.52
100	1.58	(1.70 sh)	—

sh – shoulder

to dehydration. However, in the presence of AO only minor changes in the *c*-spacing due to dehydration by the same thermal treatment were observed. From these results it may be concluded that the *c*-spacing is principally determined by the presence of the organic cation in the interlayer space. Table 1 shows that up to a degree of saturation of 50 mmole dye per 100 g clay the *c*-spacing is 1.3 nm, a monolayer of AO is formed in the interlayer space with the aromatic rings parallel to the silicate layer. With a higher degree of saturation, the *c*-spacing is greater than 1.5 nm, indicating a bilayer or tilting of the cationic dye relative to the silicate layer.

Thermal analysis

DTA curve, of the pure dye together with H_2O, CO_2 and NO_2 evolution curves, are shown in Fig. 1. The evolution of H_2O in the temperature range 350–715°, gives rise to several small exothermic peaks, whereas the evolution of CO_2 or NO_2 (between 500 and 715°) is accompanied by one strong exothermic peak at 615°, followed by a shoulder at 640° and a very small peak at 700°. The CH_3 evolution curve shows two sharp peaks at 245 and 405°, whereas the C_2H_6 evolution curve shows a very broad peak with a maximum extending between 625 and 650°.

Representative DTA curves of montmorillonite and laponite saturated with various amounts of AO are shown in Figs 2 and 3. The H_2O, CO_2 and NO_2 evolution curves are also shown in the figures. All these curves differ from those of pure AO. According to the directions of the various peaks, the DTA curves of both

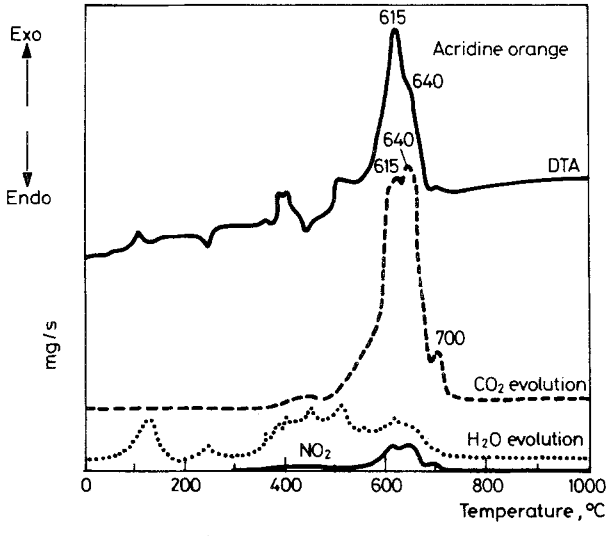


Fig. 1 DTA and gas evolution curves (CO_2, NO_2 and H_2O) of acridine orange

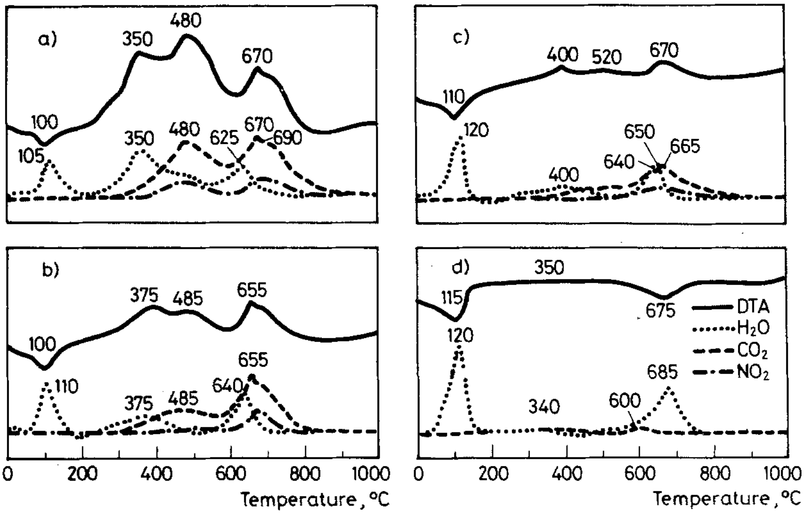


Fig. 2 DTA and gas evolution curves (CO_2, NO_2 and H_2O) of AO treated montmorillonite: a = 100, b = 50, c = 25 and d = 4 mmole AO per 100 g montmorillonite

organo-clays can be divided into three regions. From the DTG curves (not shown) it is obvious that the three regions are associated with three stages of weightloss. In the first region (region A), up to 200°, the endothermic dehydration of the clay is the major thermal reaction. The second region (region B) is between 200–575° and between 200–670° in the curves of montmorillonite and laponite, respectively. The exothermic oxidation of the adsorbed AO is the principal thermal reaction of this region. The DTG curves show that this region can be further divided into three sub-regions. The third region (region C) occurs at temperatures above 575 and 670° for montmorillonite and laponite, respectively. The major thermal reacions of this region are the dehydroxylation and recrystallization of the smectite minerals and the last stages of the oxidation of organic matter. Weightloss occurring in the different regions were determined from TG curves (Tables 2 and 3).

The first region

According to the H_2O evolution curves the first region represents the dehydration of the clay. At this stage the interlayer water is evolved. It is characterized by a single endothermic peak in the DTA curve and a single peak in the DTG curves. The peak maximum in the DTA or DTG curves shifts from 115 or 135 to 100 or 110° with each increasing degree of saturation of montmorillonite or laponite, respectively. At the same time the amount of evolved water decreases (see

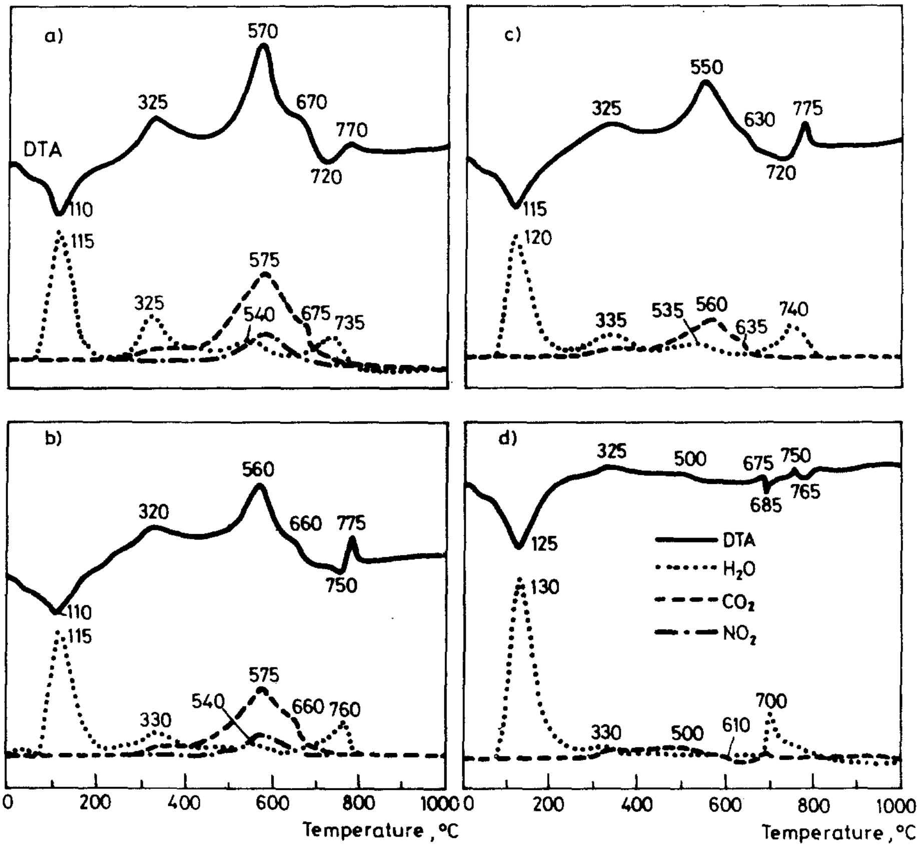


Fig. 3 DTA and gas evolution curves (CO_2, NO_2 and H_2O) of AO treated laponite: a = 75, b = 50, c = 25 and d = 4 mmole AO per 100 g laponite

Table 2 Weightloss (%) obtained by TG of montmorillonite treated with various amounts of AO in three regions (A, B and C) of the thermal analysis

mM AO per 100 g clay	Montmorillonite				
	A	B			C
	25–200 °C	200–300 °C	300–425 °C	425–575 °C	575–1000 °C
0	6.60	0.00	0.10	0.20	3.40
4	5.25	0.00	0.25	0.50	3.00
25	4.00	0.25	0.75	1.50	7.00
50	3.90	0.25	1.50	3.00	10.25
100	2.15	0.50	3.50	6.25	11.25

Table 3 Weightloss (%) obtained by TG of laponite treated with various amounts of AO in three regions (A, B and C) of the thermal analysis

mM AO per 100 g clay	Laponite				
	A	B			C
	25–200 °C	200–300 °C	300–450 °C	450–670 °C	670–1000 °C
0	11.10	1.30	0.80	1.70	2.40
4	13.75	0.50	1.25	2.00	3.00
25	9.75	0.50	1.50	5.75	3.00
50	8.00	0.25	1.75	8.75	3.25
75	8.00	0.50	2.00	10.50	3.75

H_2O evolution curves and Table 2 and 3). The shift in the peak temperature and the decrease in weightloss are probably associated with increasing hydrophobicity of the interlayer space as a result of increase in the amount of adsorbed dye. As a consequence of increasing hydrophobicity the amount of interlayer water decreases.

The second region

In the DTA curves of AO treated laponite, two exothermic peaks are traced at 320–325 (medium) and 500–570° and a shoulder at 630–670°. The location of the second peak moves to lower temperatures with decreasing degrees of saturation of the clay. It appears at 500° with a degree of saturation of 4 mmole dye per 100 g laponite. In the curves of AO treated montmorillonite peak maxima appear at 350–400 and 480–520°. The second peak is strong in comparison with the first peak only when the degree of saturation is 100 mmole dye per 100 g montmorillonite. It shifts to higher temperatures and is weak and broad with lower degrees of saturation. It is not observed with 4 mmole dye per 100 g clay. These exothermic peaks, which do not appear in the DTA curves of untreated montmorillonite and laponite, result from the oxidation of the adsorbed AO. These peaks are associated with weightloss which increases with increasing degrees of saturation (Tables 2 and 3). The H_2O which is evolved in this region results from the combination of hydrogen atoms of the AO cations with oxygen atoms of air. The H_2O evolution curves of AO treated laponite differ from those of montmorillonite, the former showing an intense peak at 325–330°, followed by a smaller peak at 535–540°, whereas the curves of the latter show a single intense peak at 350–400°. The degree of saturation has no effect on the shape and peak temperature of the H_2O evolution curves of laponite in the temperature range of the second region. On the other hand, it has an effect on the location of the peak of the H_2O evolution curve of AO-montmorillonite. It appears at 340° with 4 mmole AO per 100 g clay, shifts to 400° with 25 mmole dye and returns to 350° with 100 mmole dye per 100 g montmorillonite.

The evolution of CO_2 and NO_2 results from the oxidation of the carbon and nitrogen atoms, respectively, originating from the AO cations. The evolution curves of AO-montmorillonite show a great dependency on the degree of saturation whereas those of AO-laponite show only a slight dependency, as indicated by the location of the peaks. All evolution curves of laponite show one shoulder at 325° and an intense peak at 500–575° followed by a shoulder at 610–675°. In the case of montmorillonite, the evolution of CO_2 starts below 300°. With 4–25 mmole AO per 100 g montmorillonite the principal oxidation reaction takes place above 600° (third region). With 50 mmole AO per 100 g clay a CO_2 or NO_2 evolution peak appears at 480°. The intensity of this peak increases with each increasing degree of saturation.

Correlation of the DTA curve with the H_2O and CO_2 evolution curves reveals that the profile of the DTA curve is determined by the amounts of hydrogen and carbon which are oxidized. In the case of montmorillonite the first exothermic peak at 350–400° is the consequence of the oxidation of hydrogen atoms. The second peak at 480–520° is due to the oxidation of carbon. In the case of laponite the first exothermic peak at 325° is due to the oxidation of hydrogen atoms. The second exothermic peak at 500–570° is due to the oxidation of carbon atoms. Hydrogen atoms are also oxidized at this stage, and due to the simultaneous oxidation of both elements this exothermic peak is more intense than the first peak.

Mass 15 represents CH_3 radicals. They are characteristic of methane. The identification of these radicals in the evolved gases may serve as proof of the pyrolysis of AO. Peak maxima are located at 330–360 and 330° in the evolution curves of montmorillonite and laponite, respectively, before the maxima of peaks which characterize oxidation reactions of carbon atoms.

Mass 30 represents C_2H_6 and NO. The identification of the former among the evolved gases may serve as a proof of pyrolysis. NO is obtained due to the incomplete oxidation of nitrogen atoms of the AO. Peaks in the gas evolution curves of mass 30 are much more intense than those of mass 15. Representative gas evolution curves of mass 30 are given in Fig. 4. From the figure it is obvious that the degree of saturation has an effect on the shape of the curves in the case of montmorillonite and no effect in the case of laponite. The first peak in the gas evolution curves of montmorillonite and laponite is located at temperatures slightly less than the temperatures of the first peak in the CH_3 evolution curves and less than those of the peaks of the oxidation reactions. It probably characterizes the pyrolysis of AO. The last peak in these evolution curves may represent, at least in part, the

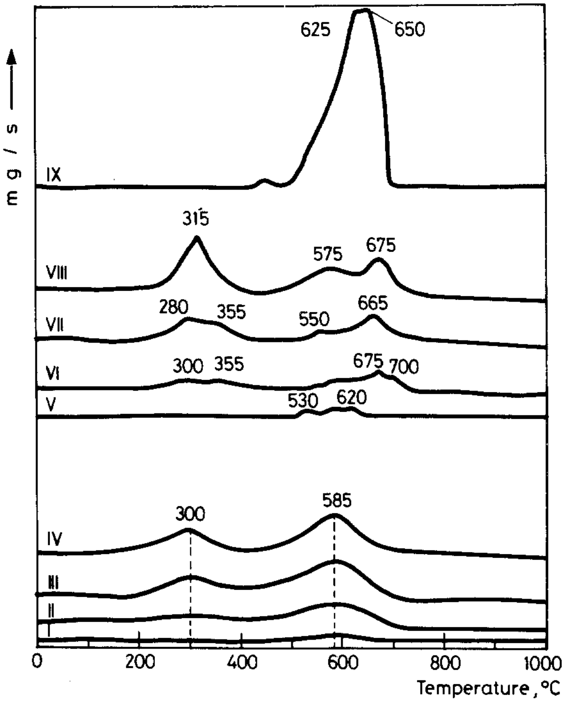


Fig. 4 Gas evolution curve of mass 30 (C_2H_6 and NO) of pure AO and of AO treated laponite and montmorillonite. I = 4, II = 25, III = 50, IV = 75 mmole AO per 100 g laponite; V = 4, VI = 25, VII = 50, VIII = 100 mmole AO per 100 g montmorillonite and IX = pure AO

incomplete oxidation of the nitrogen. The temperature of this peak is slightly above that of the last peak of the CO_2 evolution curve.

Weightloss in the temperature range 300–425 and 300–450° in the TG of AO-montmorillonite and AO-laponite, respectively, is mainly due to the combination of the hydrogen atoms with oxygen atoms of air. In the case of laponite only part of the hydrogen is oxidized at this stage and weightloss increases very little with increasing degrees of saturation (Table 3). The remaining hydrogen is oxidized at 540°.

Weightloss in the temperature range of 425–575 and 450–670° in the TG of AO-montmorillonite and AO-laponite, respectively, is due to the combination of carbon atoms with oxygen atoms of air. In the case of laponite weightloss increases significantly with increasing degrees of saturation. In the case of montmorillonite, weightloss increases to a smaller extent with increasing degrees of saturation, indicating that only part of the carbon is oxidized at this stage. In the discussion about the third region of the DTA curve, it will be shown that the oxidation of the residual carbon in montmorillonite occurs above 600°.

The third region

This region represents the dehydroxylation of the smectite minerals. The DTA curve of untreated montmorillonite shows an endothermic peak at 695°. In the case of untreated laponite the dehydroxylation occurs simultaneously with a recrystallization reaction. A broad endothermic peak is recorded at 730°, followed by a sharp exothermic peak at 755°.

Tables 2 and 3 show that the degree of saturation has almost no effect on the thermal weightloss of AO-laponite at the temperatures of the third region, but affects the thermal weightloss of AO-montmorillonite. In the latter, weightloss during the third region increases with each increasing degree of saturation, indicating that the oxidation of organic matter has not been completed in the second region but continues into the third region. In agreement with this, the CO_2 and NO_2 evolution curves of montmorillonite show two peaks at 640–670 and 665–690°. However, weightloss at this stage increases only up to a degree of saturation of 50 mmole AO per 100 g montmorillonite. With higher degrees of saturation the increment in weightloss becomes very small. It should be mentioned here that with a high degree of saturation a large portion of carbon is oxidized during the period of the second region of the thermal analysis.

In AO treated montmorillonite the exothermic oxidation reaction overlaps the endothermic dehydroxylation reaction (compare H_2O and CO_2 evolution curves in Fig. 2). An endothermic peak is shown in the DTA curve of montmorillonite saturated with 4 mmole AO per 100 g clay. On the other hand, with 25, 50 and 100 mmole AO per 100 g montmorillonite exothermic peaks are detected in this region (Fig. 2).

The temperature of the dehydroxylation of montmorillonite can be determined from the H_2O evolution curve. It is located at 695° in the H_2O evolution curve of untreated montmorillonite. Figure 2 shows that the dehydroxylation peak shifts to lower temperatures with increasing degrees of saturation. It is located at 680 and 625° with 4 and 100 mmole dye per 100 g montmorillonite, respectively.

Comparison of thermal analysis curves of AO treated clays with those of R6G treated clays

1. The exothermic peaks of DTA curves of montmorillonite or laponite treated with R6G or AO and recorded in air are due to the oxidation of H, C and N atoms. The first exothermic peak is the result of the oxidation of the H atoms, whereas the other peaks result from the oxidation of C and N atoms.

2. The shapes of the gas evolution curves of R6G treated montmorillonite or laponite are not affected by the degree of saturation of the clay. This may indicate that only one type of association is obtained between R6G and montmorillonite

and one type between R6G and laponite. Both these associations are independent of the degree of saturation.

The shape of the gas evolution curves of AO treated laponite is independent of the degree of saturation of the clay, indicating that only one type of association is obtained between AO and laponite. On the other hand, gas evolution curves of AO treated montmorillonite showed that the shapes of the different curves and the appearance of several peaks depend on the degree of saturation of the clay. This is an indication of the presence of several types of association between the dye and montmorillonite.

3. During the thermal analysis of AO- or R6G-laponite most of the organic matter is oxidized before the dehydroxylation of the clay, whereas with AO- or R6G-montmorillonite a large portion of the organic matter is oxidized only during the dehydroxylation of the clay.

4. Pyrolysis products such as CH_3 and C_2H_6 were detected in the gaseous phase, in spite of being thermal-analyzed in an oxidizing atmosphere. With R6G treated clays CH_3 was the principal pyrolysis product whereas with AO treated clays C_2H_6 was the principal pyrolysis product.

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The authors wish to thank Dr. Harold Cross for reading the manuscript and for his useful discussions and suggestions. The X-ray diffractions were recorded by Mr. Shlomo Meiri of the Department of Geology at the Hebrew University of Jerusalem. His assistance is gratefully acknowledged. Our thanks to Laporte Industries, England for the kind donation of the laponite sample.

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Zusammenfassung — Parallel mit den DTA-, TG- und DTG-Kurven wurden auch die H_2O-, CO_2-, NO_2-, CH_3- und C_2H_6-EGA-Kurven von mit verschiedenen Mengen Akridinorange behandelten Montmorillonit- und Laponitproben in Luft bestimmt. Die Thermoanalysendiagramme können in drei Regionen unterteilt werden: die Dehydration der Tonerde, die Oxydation des organischen Kations und die Dehydroxylierung der Tonerde. Die Oxydationsregion beinhaltet zwei exotherme Peaks, die die Oxydation von H und C der organischen Substanz repräsentieren. Die Thermoanalysendiagramme von Montmorillonit unterscheiden sich von denen von Laponit. Im Gegensatz zu Montmorillonit werden die EGA-Kurven von Laponit nicht durch den Grad der Sättigung der Tonerde mit Farbstoff beeinflußt.

Резюме — В атмосфере воздуха были измерены ДТА, ТГ и ДТГ кривые монтмориллонита и лапонита, обработанных различными количествами красителя акридинового оранжевого. Одновременно были измерены кривые АВГ для воды, двуокиси углерода, двуокиси азота, метана и этана. Термические кривые могут быть разделены на три области, представляющие дегидратацию минерала, окисление органического катиона и дегидроксилирование минерала. Область окисления показывает два экзотермических пика, обусловленные окислением водорода и углерода органического вещества. Термические кривые лапонита отличаются от таковых для монтмориллонита. Профиль кривых АВГ лапонита не зависит от степени насыщения минерала красителем, тогда как таковые для монтмориллонита затрагиваются степенью насыщения его красителем.