

ALKYLAMMONIUM DECOMPOSITION ON MONTMORILLONITE SURFACES IN AN INERT ATMOSPHERE

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Abstract—A study of the thermal transformation of alkylammonium cations adsorbed on the surface of a montmorillonite in various conditions of hydration has been carried out. The experimental conditions were: inert atmosphere, temperatures below 250°C and time periods up to 270 days. The reactions observed are mainly transalkylations, for which a mechanism of acid catalysis is proposed. A high degree of dissociation of the water remaining on the surface of the clay is required and is attained for an optimal, and rather low, water content of the clay.

INTRODUCTION

RECENT work by Calvet *et al.* (1964) has shown it is possible for alkylammonium cations adsorbed on montmorillonite surface to be transformed at temperatures considerably below the theoretical decomposition temperatures of amines or of their chlorhydrates. Above 100°C, the cations decompose into NH_4^+ (which remains on the clay), organic residues and hydrocarbons. The observations were interpreted to be the result of catalytic rupture of the C–N bond. The catalytic effect was attributed to protons of the water adsorbed on the montmorillonite surface.

The present study re-examines these experiments in an inert atmosphere (they were also made in the presence of oxygen) and with much longer time periods. Attention is also paid to the mechanism of the reactions and to the quantitative aspects of the phenomena, and especially to the actual possibilities of generation of hydrocarbons. In this way, the work aims to investigate some of the properties of clay surfaces under mild experimental conditions so as to give further insight on the nature of a possible catalytic activity of clays in sediments.

EXPERIMENTAL

Material

The montmorillonite clay mineral is from Camp Berteau, Morocco. Its chemical composition is $(\text{Si}_8)^{\text{IV}}(\text{Al}_{3-1}\text{Fe}_{0-25}\text{Mg}_{0-67})^{\text{VI}}\text{O}_{20}(\text{OH})_4$ and its specific

surface area is approximately 700 m²/g (Fripiat *et al.*, 1962).

Its preparation begins by a mineralogical purification which is achieved in the following way:

The clay is stirred for four hr in a solution of sodium chloride 1 N, with 20g of clay per liter of solution, then recovered by centrifugation. The entire operation is then repeated.

The clay is then washed until chlorides have disappeared from the rinse water. The fraction lower than 2 μ diameter is separated according to the time of sedimentation or centrifugation. This fraction is treated by a 10% hydrogen peroxide solution at 80–90°C, in order to destroy the small amounts of organic matter, i.e. approximately 0.5% wt, naturally associated with the clay. After drying in an oven at 180°C during several hours, the recovered fraction is finely crushed and sieved. The material thus obtained has the following characteristics:

no impurity can be found by X-ray diffraction
the C.E.C. is about 120 meq for 100g of montmorillonite heated at 1200°C (determination made by exchange with cobaltihexammine 0.05 N and colorimetry at 468 m μ)
the carbon content is less than 0.05% wt
the fraction below 1 μ represents two-thirds, and that below 2 μ , 99% wt of the solid sample.

The clay obtained above is suspended (20 g/l.) in a 0.5 N solution of the analytically pure chloride or bromide salt of the organic cation. The suspen-

sion is stirred for 4 hr. After recovery of the clay by centrifugation, the operation is repeated. The clay is then washed until all chlorides or bromides disappear, and then it is dried in air at room temperature. The saturation is checked by measuring the organic carbon contained or by the microkjeldahl procedure. The following cation exchange capacities (in meq per 100g of montmorillonite calcined at 1200°C) were obtained:

Ammonium clay : 125
 Methylammonium clay : 125
 Dimethylammonium clay : 130
 Trimethylammonium clay : 127
 Ethylammonium clay : 127
 Diethylammonium clay : 120
 Triethylammonium clay : 115
 Tetraethylammonium clay : 109

The products obtained by heating the organo-clay complexes were analyzed by gas chromatography and i.r. spectroscopy. The carbon balance was also determined for each quantitative experiment, and cation exchange capacity measurements were made at different stages of the operation.

Chromatographic examination

A small amount (several g) of the air-dried clay-organic complex to be studied was introduced into a 25 ml Pyrex reactor. This reactor was exposed to the desired atmosphere and sealed.

Most experiments were conducted under 30 mbar of water-vapor pressure: the reactor had then a cold finger filled with water, the temperature of which was kept at 25°C.

Other experiments were conducted either with very low water-vapor pressure or with high water-vapor pressure: very low water-vapor pressure was obtained by dehydration of the clay under vacuum inside the reactor before sealing, until disappearance of the water deformation band as established by i.r. spectroscopy studies. The reactors used for this purpose also had a cold finger.

Obtaining a high pressure of water vapor was achieved in the following way: a convenient amount of water was put inside the reactor before sealing. By heating at the temperature chosen for the experiment (160°–220°C), water-vapor pressure grew up to a value near of the saturating water-vapor pressure at this temperature. Breackage of the reactor was prevented by enclosing it inside a hermetic metal container and putting a small amount of water between the wall of the reactor and the wall of the container. In this way the water-vapor pressure was about the same inside and outside the Pyrex reactor when it was heated.

After the end of an experiment, both the gas in the reactor and the products fixed on the clay were analysed: the gaseous phase of the reactor was transferred into a container initially filled with mercury via a Toepler pump and then analysed by gas chromatography. On the basis of the experimental results, only the C₁–C₇ hydrocarbons were subjected to a systematic search. A 4 m × 1/8 in column of chromosorb Pdmcs 60/80 coated with 20% DC 200 was used for this purpose (injector and detector at room temperature, detection by flame ionization, isothermal run at 60°C).

The decomposition products in the solid phase were examined as follows: an aliquot of the clay was extracted by chloroform or a mixture of methanol, acetone and benzene (15/15/70). The solvent was then analyzed by gas chromatography in a 1.5 m × 1/8 in column with 15% SE 30 on Aeropak by temperature programming from 50 to 300°C (injector and detector at 140°C, detection by flame ionization). A second portion (1g) of the clay was stirred for four hours in 50ml of a 0.05N cobaltihexammine chloride solution. After centrifugation, an aliquot of the solution was sampled and treated with concentrated soda or potash to set free all the organic bases, then analyzed by gas chromatography. On the basis of the experimental results, a systematic search for amines and simple aliphatic alcohols was carried out by means of a 3 m × 1/8 in column with 20% Dowfax 9N9+2.5% NaOH on chromosorb P 60/80 at 95°C (injector and detector at 200°C, detection by flame ionization).

It would have been interesting to titrate the desorbed ammonium and the quaternary aliphatic ammonium compounds in the eluent solutions. For the former, this was not possible since free ammonia cannot be detected by flame ionization. The use of another detector causes a loss of sensitivity so that the method described becomes inapplicable. As it will be seen, spectroscopic methods overcome this disadvantage to a certain extent. With regard to quaternary ammonium compounds, which do not produce volatile compounds by the addition of a base, the method described is inadequate.

Investigations by i.r. spectroscopy

The clay organic complex to be studied was suspended in water (1g/10ml). Several drops were evaporated on a Mylar foil. The solid clay film was then peeled off with a razor blade or on the edge of a glass slide. It was then fixed on a metal holder which was placed in a cell fitted with NaCl windows similar to that described by Uytterhoeven (1965). The cell was attached to a vacuum line so

that the sample could be put under a controlled atmosphere. The cell may be heated to the desired temperature and then turned upside down so that the sample holder slides in front of the NaCl windows. In this way the spectra can be recorded at regular intervals during heating. Water-vapor pressure can be maintained in the system as long as it remains moderate. By comparison with the evolution experiment in a sealed reactor, this technique has the advantage of consuming very little material and of enabling the thermal decomposition to be followed during the experiment.

I.R. spectroscopy was also used to supplement the chromatographic techniques for ammonium determination in the desorption solution. For this, after heating the reactor, a sample of the complex is desorbed by potassium bromide. An aliquot of the desorption solution is evaporated. The solid mixture recovered, which is mainly potassium bromide, is then pressed into pellets and examined by i.r. spectroscopy (P. Cloos, private communication); the presence of ammonium is indicated by the NH_4^+ absorption band at 1428 cm^{-1} .

I.R. SPECTROSCOPY RESULTS

The experiments were made under pressure of 1 bar of helium with durations ranging up to 100 hr and temperatures from 95° to 220°C . The following complexes were studied: methyl, dimethyl and trimethylammonium montmorillonites; ethyl, diethyl and triethylammonium montmorillonites. Spectral variations during heating were followed under two different conditions of hydration: under a water pressure of 30 mbar, and after dehydration respectively. The spectra of the mono and dialkylated complexes have the characteristic bands listed in Tables 1 and 2.

A detailed discussion of the assignment of these bands and of their individual features has been published previously (Fripiat *et al.*, 1969).

The monoalkylated complexes reveal a band that is characteristic of the NH_3^+ group at 1515 cm^{-1} . For the dialkylated complexes the weak deformation band of the NH_2^+ group at 1623 cm^{-1} is characteristic but it may be confused with the deformation band of water and can be observed conveniently after dehydration only. The trialkylated complexes have a very weak NH^+ deformation band and, consequently, the spectra have no very characteristic features.

Transformations under a water pressure of 30 mbar (see Figs. 1 and 2)

Monoalkylated complexes. On heating, the following features are observed: the gradual disappearance of the deformation band of NH_3^+ at 1515 cm^{-1} , the appearance of the deformation band

Table 1. Assignments of i.r. absorption bands: methylammonium montmorillonites

Methylammonium montmorillonite					
Outgassed at 25°C and then exposed to 24 nm Hg water vapour			Outgassed at 25°C		
$\nu(\text{cm}^{-1})$	Assign.	<i>I</i>	$\nu(\text{cm}^{-1})$	Assign.	<i>I</i>
1428	$\delta(\text{NH}_3^+)$ wag	W	1428	$\delta(\text{NH}_3^+)$ wag	W
1466	$\delta_a(\text{CH}_3)$	S	1466	$\delta_a(\text{CH}_3)$	S
			1488	$\delta_s(\text{NH}_3^+)$	S
1515	$\delta_s(\text{NH}_3^+)$	S			
1623	$\left\{ \begin{array}{l} \delta(\text{H}_2\text{O}) \\ \delta(\text{NH}_3^+) \end{array} \right.$	S			
2777	$\nu_s(\text{NH}_3^+)$		2777	$\nu_s(\text{NH}_3^+)$	
2857	$\nu_s(\text{CH}_3)$	W	2857	$\nu_s(\text{CH}_3)$	W
2941	$\nu_a(\text{CH}_3)$	W	2941	$\nu_a(\text{CH}_3)$	W
3048	$\nu_a(\text{NH}_3^+)$	W	3048	$\nu_a(\text{NH}_3^+)$	W
3105	$\nu(\text{N-H})$	V.S	3105	$\nu(\text{N-H})$	V.S
Dimethylammonium montmorillonite					
			1404	$\delta_s(\text{CH}_3)$	W
1428	$\delta(\text{NH}_2^+)$ wag	W	1418	$\delta(\text{NH}_2^+)$ wag	W
1470	$\delta_a(\text{CH}_3)$	V.S	1470	$\delta_a(\text{CH}_3)$	M
1626	$\left\{ \begin{array}{l} \delta(\text{NH}_2^+) \\ \delta(\text{H}_2\text{O}) \end{array} \right.$	S	1626	$\delta(\text{NH}_2^+)$	
2500	N-H-Cl				
2809	$\nu_s(\text{CH}_3)$	V.S	2841	$\nu_s(\text{CH}_3)$	S
2915	$\nu_a(\text{CH}_3)$	W	2915	$\nu_a(\text{CH}_3)$	V.S
3067	$\nu(\text{C-H})$				
			3200	$\nu(\text{N-H})$	V.S

W—weak; Sh—shoulder; S—strong; V.S—very strong; M—mean.

of NH_4^+ at 1428 cm^{-1} and the reinforcement of a NH^+ stretching vibration band at 3257 cm^{-1} .

If the film is highly dehydrated under vacuum after the heating cycle, the persistence of an absorption band at 1623 cm^{-1} , i.e. at the frequency of the NH_2^+ deformation band, is noticeable. However the interference of NH_2^+ band and H_2O band may be confusing, though there is a definite shift between the two bands (Fig. 2). The intensity of the CH_3 and CH_2 bands undergoes no significant modification.

The i.r. spectroscopic observation of the desorbed material diluted into a pellet of potassium bromide (see investigation by i.r. spectroscopy) confirms the formation of the ammonium cation.

Under the experimental conditions, the NH_3^+ band never entirely disappears and the intensity of the NH_4^+ band evaluated by comparison with ammonium montmorillonite, remains less than the corresponding intensity at 50% of saturation.

Dialkylated complexes. The weak intensity of the NH_2^+ deformation band and its interference with the water deformation band make observations more difficult here. Nevertheless, it can be observed that: a NH_3^+ band appears at 1515 cm^{-1} , a NH_4^+ band appears, although more slowly than

Table 2. Assignments of i.r. absorption bands: ethylammonium montmorillonites

Ethylammonium montmorillonite			Ethylammonium montmorillonite		
Outgassed at 25°C			Outgassed at 25°C		
and then exposed to 24 mm Hg water vapour					
$\nu(\text{cm}^{-1})$	Assign.	I	$\nu(\text{cm}^{-1})$	Assign.	I
1401	$\delta_s(\text{CH}_3)$	S	1401	$\delta_s(\text{CH}_3)$	S
1460	$\delta_a(\text{CH}_3)$	W	1458	$\delta_a(\text{CH}_3)$	W
1475	$\delta(\text{CH}_2)$	W	1475	$\delta(\text{CH}_2)$	W
			1488	$\delta(\text{NH}_3^+)$	S
1511	$\delta(\text{NH}_3^+)$	W			
1626	$\delta(\text{H}_2\text{O})$	S	1608		
2840	$\nu_s(\text{CH}_3)$	W			
2840	$\nu(\text{CH}_2)$	W			
3077	$\nu(\text{N-H}^+)$				
3247					
Diethylammonium montmorillonite					
1360		W	1366		
1379		W			
1390	$\delta_s(\text{CH}_3)$	S	1391	$\delta_s(\text{CH}_3)$	V.S
			1420	$\delta(\text{NH}^+)$	Sh
1460	$\delta_a(\text{CH}_3)$	S	1453	$\delta_a(\text{CH}_3)$	W
1477	$\delta(\text{CH}_2)$	Sh	1481	$\delta(\text{CH}_2)$	W
	$\delta(\text{H}_2\text{O})$				
1635	$\delta(\text{NH}_2^+)$	S	1623	$\delta(\text{NH}_2^+)$	W
2500	(N-H-Cl)	W	2500	(N-H-Cl)	W
2860	$\nu_s(\text{CH}_3)$	M	2850	$\nu_s(\text{CH}_3)$	W
2890	$\nu(\text{CH}_2)$	W	2900	$\nu(\text{CH}_2)$	W
			2932		W
2990	$\nu_a(\text{CH}_3)$	S	2976	$\nu_a(\text{CH}_3)$	
3060		W			
3180	$\nu(\text{N-H}^+)$	S			

W—weak; Sh—shoulder; S—strong; V.S—very strong; M—mean.

for monoalkylated complexes, the CH_2 and CH_3 bands do not change.

Trialkylated complexes. No significant modification in the spectra is observed.

Observation in the absence of water. The film is dehydrated under vacuum inside the cell for a period long enough to cause the disappearance of the H_2O deformation band. Dry helium is then reintroduced. The following facts are observed; (a) before heating there is a displacement of the NH_3^+ band of the monoalkylated complexes as well as a change in the intensity of the CH_3 and CH_2 deformation bands. This phenomenon is reversible by rehydration (Fripiat *et al.*, 1969); (b) no significant change occurs in the spectra during heating.

CHROMATOGRAPHIC RESULTS

Whereas the examination by i.r. spectroscopy proves the existence of reactions on the surface of the clay and reveals the importance of the role

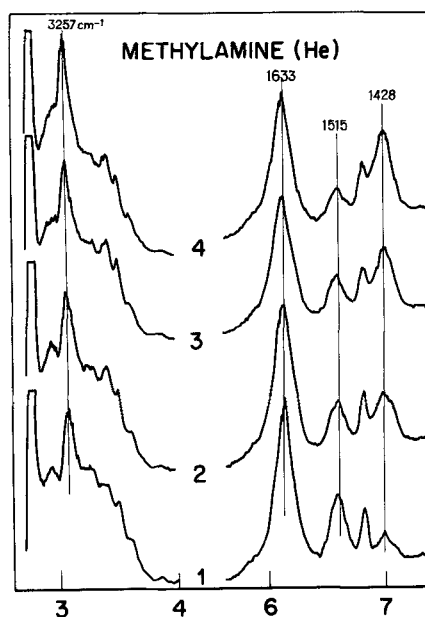


Fig. 1. Spectra of methylammonium montmorillonite heated to 185°C in helium with 30 m.b. water pressure. (1)—After 30 mn of heating; (2)—After 20 hr of heating; (3)—After 35 hr of heating. (4)—After 100 hr of heating.

played by water, it does not give sufficient information about the nature of these reactions. Therefore, the chromatographic analysis of the organic material in the solid phase and in the gaseous phase were performed as well as the carbon analysis and the cation exchange capacity at different stages of the transformation. These determinations were carried out mainly on the ethyl-, diethyl-, triethyl- and tetraethylammonium montmorillonites under the following experimental conditions: 10 g of clay placed in a sealed reactor under a pressure of 1 bar of helium; temperatures from 160° to 240°C; duration, 24–720 hr. The water pressure was mainly maintained at 30 mbar, but several experiments were made under different water-vapor pressure. Additional experiments were made on methylammonium montmorillonites as well as on ethylamines and ethylamine chlorhydrates.

Transformation of ethylammonium montmorillonites under a water pressure of 30 mbar.

The effect of the thermal treatment on the C.E.C. as measured by exchange with a 0.05N cobalt-hexammine chloride solution. The desorption process of unheated ethylammonium montmorillonites is shown in Fig. 3. Measurements were made, twice for each concentration by exchange with cobalt-hexammine cation, followed by colorimetry at 468m μ . The results were confirmed by the

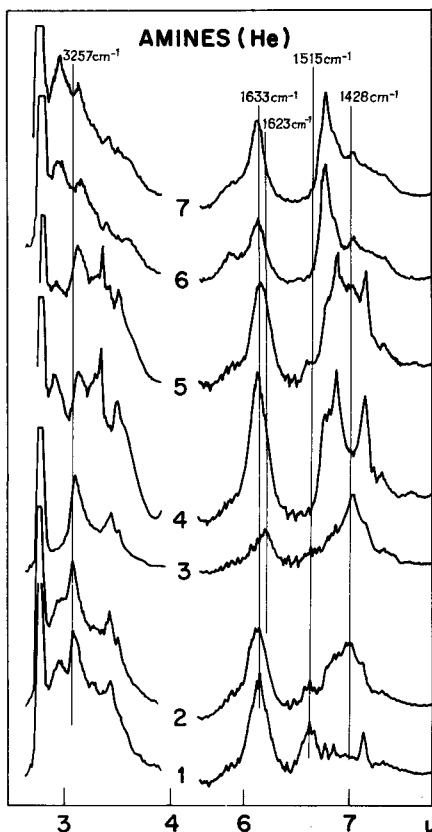


Fig. 2. Spectra of alkylammonium montmorillonites heated to 220°C in helium with 30 mbar water pressure. (1)–Ethylammonium montmorillonite, not heated; (2)–Ethylammonium montmorillonite, after 80 hr of heating; (3)–Ethylammonium montmorillonite, after 70 hr of heating, then vacuum dehydration; (4)–Diethylammonium montmorillonite, not heated; (5)–Diethylammonium montmorillonite, after 60 hr of heating; (6)–Triethylammonium montmorillonite, not heated; (7)–Triethylammonium montmorillonite, after 60 hr of heating.

carbon analysis of the clay after the exchange. The exchange isotherms of ethyl- and diethylammonium cations are quite similar to that obtained for ammonium.

Triethylammonium is more difficult to desorb. Its elimination requires three successive exchanges in 0.05N solution.

The complete desorption of tetraethylammonium is almost impossible as shown by curves 6 and 6' in Fig. 3. The following values of residual carbon are found for three successive exchanges by 0.05N solutions (initial value of 10.4%): 4.8% after one exchange, 3.7% after two exchanges, 2.7% after three exchanges.

After three successive exchanges, the ethyl-diethyl and triethylammonium cations are thus

eliminated and about one fourth of the tetraethylammonium remains.

Table 3 shows that after heating at 160°C, the desorption of ethyl- and diethylammonium montmorillonites is almost total after one exchange in a 0.05N solution but it tends to become more difficult to remove after heating at 200°C. For triethylammonium montmorillonite desorption is much less complete, even after heating at 160°C. Likewise, as shown in Fig. 3, its desorption behavior becomes similar to that of tetraethylammonium montmorillonite. Desorption is favored by heating the tetraethylammonium montmorillonite and its exchange capacity increases.

Chromatographic analysis of the desorbed organic phase

In the cobaltihexammine chloride desorption solutions, ethyl, diethyl and triethylammonium ions are found in varying proportions depending on the cation initially fixed to the clay and on the experimental conditions (see Fig. 5A). Moreover, i.r. spectroscopy shows the presence of ammonium in desorption solutions in the case of ethyl and diethylammonium montmorillonites, its concentration being higher in the former than in the latter case. Table 4 shows the relative proportions observed for the three cations analyzed, expressed in % carbon.

From these results the existence of transalkylation reactions appears as evident.

Carbon balance. The organic carbon content of ethylammonium montmorillonite was measured before and after heating and also after three successive exchanges in 0.05N cobaltihexammine chloride solutions. These data are shown in Table 5. Simultaneously other solvents were used (distilled water, chloroform, mixture of methanol, acetone and benzene in the proportion 15–15–70) but these extractions did not result in any significant change in the amount of residual organic carbon, and the chromatographic analysis of these solvents gave similar results before and after extraction.

An examination of Table 5 brings out the following points: (a) after heating and before desorption, there is a significant loss of carbon in the case of tetraethylammonium–montmorillonite only. Most of the carbon is in a cationic form since most of it can be removed by three successive treatments with the cobaltihexammine solution, whereas extractions with non-cationic solvents have no effect. (b) in the case of triethylammonium and tetraethylammonium montmorillonites noticeable amounts of non-desorbed carbon still remain. This carbon cannot entirely be attributed to the presence of tetraethylammonium, since in some cases more

Table 3. Extraction by a 0.05N cobaltihexammine chloride solution, after the indicated thermal treatment. The results are in meq/100 g of montmorillonite heated at 1200°C

Time Temp.	Initial value	Ethylammonium Mt			Diethylammonium Mt			Triethylammonium Mt			Tetraethylammonium Mt			
		24 hr	77 hr	240 hr	720 hr	Initial value	77 hr	720 hr	Initial value	77 hr	720 hr	Initial value	77 hr	720 hr
160°C	128	127	127	129	127	122	121	116	85	83	79	60	62	69
200°C	128	126	124	121	121	122	116	113	85	75	76	60	70	78
220°C	128	125	121	121	119	122	110.5	105	85	78	74	60	75	72

Note. Initial exchange capacity of ammonium montmorillonite = 125 meq/100 g, of ethylammonium montmorillonite = 127 meq/100 g, of diethylammonium montmorillonite = 120 meq/100 g, of triethylammonium montmorillonite = 115 meq/100 g, and of tetraethylammonium montmorillonite = 109 meq/100 g.

Table 4. Amines Analysed on Dowfax 9N9 - Measurements for: (I) Ethylammonium montmorillonite; (II) Diethylammonium montmorillonite; (III) Triethylammonium montmorillonite; (IV) Tetraethylammonium montmorillonite

I	II	III	IV	Time Temp.	180°C			160°C			200°C			220°C		
					EA	DEA	TEA	EA	DEA	TEA	EA	DEA	TEA	EA	DEA	TEA
I	II	III	IV	24 hr	90.0	10.0		98.7	1.3		62.5	67.5		23.8	72.6	0.9
				77 hr	77.4	23.6	96	4	31	66.5	66.5	0.7	16.8	76.5	5.5	
				240 hr			89	11	16.8	79.5	2	14.7	72.3	11.6		
				720 hr			69.9	30.1	*	15.6	76.3	7.2	13.6	70.5	14.4	
II	III	IV	I	77 hr			2	95.5	2.5	6.4	74	19.6	8	60	32	
				720 hr			5.7	80.6	13.7	6.7	58.6	34.7	4.75	42.6	52.65	
III	IV	I	II	77 hr			9.8	6.1	93.9	*	16.3	83.7	*	18.8	81.2	
				720 hr			76	13.2	76	5.9	22.2	71.8	14.2	28.2	57.6	
IV	I	II	III	77 hr			9.7	9.7	90.3	*	7.4	92.6	0.4	11.3	88.3	
				720 hr			5.8	5.8	94.2	0.9	15.9	83.2	2.7	29.7	67.6	

The measurements for alkylammonium clays heated at different temperatures are expressed in % carbon in the mono-, di-, and triethylammonium forms.

Note. EA - Ethylammonium cation; DEA - Diethylammonium cation; TEA - Triethylammonium cation; * = traces.

Table 5. Measurements of the carbon content after heating, in weight percentage of carbon referring to clay heated at 1200°C

	Ethylammonium Mt			Diethylammonium Mt			Triethylammonium Mt			Tetraethylammonium Mt					
	Initial value	24 hr	77 hr	240 hr	720 hr	Initial value	77 hr	720 hr	Initial value	77 hr	720 hr	Initial value	77 hr	720 hr	
160°C	1	3.04	3.21	2.89	2.96	2.99	5.68	5.42	5.64	8.27	8.59	8.67	10.49	10.44	10.14
	2	0.11	0.26	0.26	0.31	0.26	0.11	0.16	0.22	0.21	0.95	1.93	2.75	2.91	2.94
200°C	1	3.04	3.05	3.03	2.95	2.97	5.68	5.38	5.60	8.27	8.55	8.76	10.49	9.69	8.66
	2	0.11	0.26	0.39	0.37	0.31	0.11	0.25	0.49	0.21	2.36	2.99	2.75	2.71	2.67
220°C	1	3.04	2.91	2.95	2.96	2.94	5.68	5.36	5.64	8.27	8.34	7.93	10.49	8.53	8.69
	2	0.11	0.31	0.38	0.40	0.52	0.11	0.42	0.87	0.21	2.67	3.42	2.75	2.17	3.73

Note. The sodium montmorillonite used as starting material contained 0.06% carbon. Measurement No. 1 corresponds to the amount of organic carbon after heating as indicated. Measurement No. 2 is obtained after three successive desorptions by a 0.05N cobaltfhexamine chloride solution.

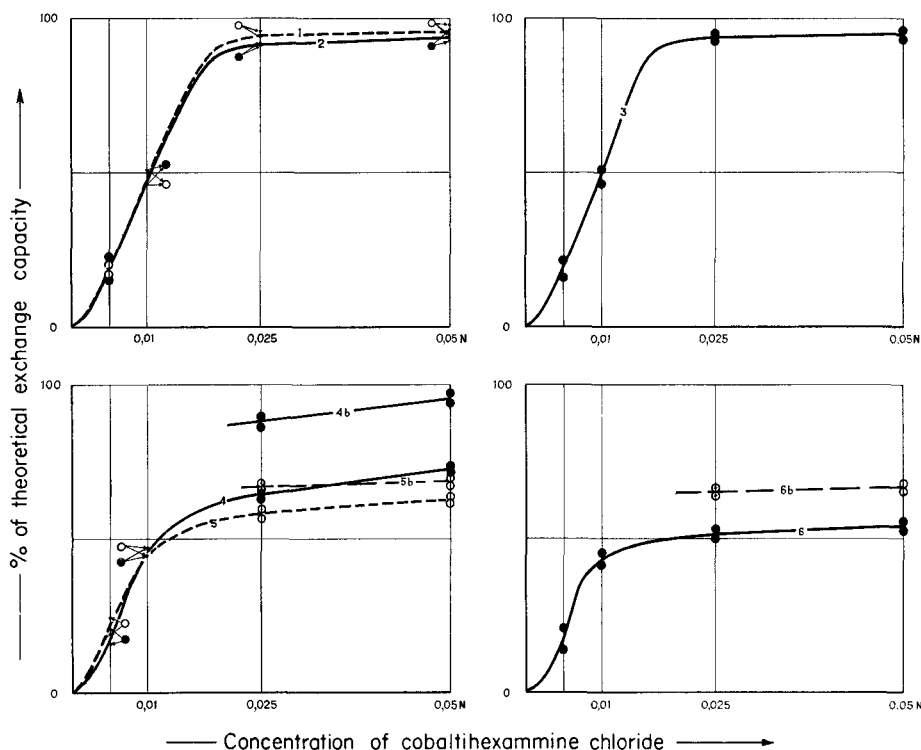


Fig. 3. Curves for exchanges by cobaltihexammine at increasing ionic forces. (1)—Diethylammonium montmorillonite; (2)—Ammonium montmorillonite; (3)—Ethylammonium montmorillonite; (4)—Triethylammonium montmorillonite; (4b)—Ditto, after a second desorption; (5)—Triethylammonium montmorillonite heated for 77 hr at 200°C; (5b)—Ditto after a second desorption; (6)—Tetraethylammonium montmorillonite; (6b)—Ditto after a second desorption. Experimental points for the following ionic forces: 0.005, 0.01, 0.025 and 0.05N.

than 25% of the initial carbon content remains after three exchanges in cobaltihexammine chloride.

Chromatographic study of the gas phase. The gaseous phase contains very small amounts of hydrocarbons, except in the case of tetraethylammonium montmorillonite. These hydrocarbons are mainly unsaturated hydrocarbons, ethylene being the most clearly represented (see Fig. 4).

The experimental results are shown in Table 6; they are expressed in micrograms of carbon in the gas phase by grams of carbon initially present in the clay.

Transformation of ethylammonium montmorillonites under other hydration conditions

Experiments were carried out with ethylammonium montmorillonite either highly dehydrated or under a high water-vapor pressure (see Experimental). An examination of the 0.05N cobaltihexammine chloride desorption products shows that the dehydration of the organo-clay complex

prevents the transalkylation reactions from occurring. We must remember that this result was suggested by i.r. spectroscopy. An excess of water inhibits also the transalkylation process. In this case, traces of ethanol in the desorption solutions are observed. As far as the hydrocarbons formation is concerned, smaller amounts are produced in the absence of water than under the water pressure of 30 mbar normally used.

Examination of methylammonium montmorillonites. Tetramethylammonium montmorillonite was not studied. For the other members of the series, the existence of transalkylation reactions was observed as for ethylammonium montmorillonites. The formation of hydrocarbons, however, is much less (see Table 7).

Comparison of the alkylammonium montmorillonites transformation with the corresponding process in pure amine chlorhydrates and amines

This comparison reveals that the amount of

Table 6. Amounts of hydrocarbons produced, in micrograms per gram of organic carbon initially fixed on clay

Temp. Time	Ethylammonium montmorillonite				Diethylammonium montmorillonite				Triethylammonium montmorillonite				Tetraethylammonium montmorillonite			
	C ₁	C ₂	C ₃	C ₄	C ₁	C ₂	C ₃	C ₄	C ₁	C ₂	C ₃	C ₄	C ₁	C ₂	C ₃	C ₄
24 hr	10	400	2													
160°C																
24 hr	60	100	traces													
200°C																
24 hr	800	1700	1200	200	30											
220°C																
77 hr	10	20	traces		5	10	1		10	200	3	traces		1700	?	3
160°C																
77 hr					20	100	10		30	5200	100	300	10	?	134000	100
200°C																
77 hr	100	100	50	traces	80	700	100	10	traces	80	13800	300	500	20		
220°C																
240 hr	50	200	20	traces												
160°C																
240 hr	500	500	500	100	30											
200°C																
240 hr	700	1000	1500	?	?											
220°C																
720 hr	100	40	3		20	20	4	traces	10	2200	10	30	traces	100	72500	70
160°C																
720 hr	800	300	100	10	80	900	50	10	50	8700	150	400	20	100	232000	1400
200°C																
720 hr	700	1000	300	60	20	200	6500	500	200	40	21200	1000	2400	300		
220°C																

Abbreviations. C₁—Methane; C₂—Ethylene; C₃—Propylene; C₄—Total C₄ olefins; C₄₊—Olefins above C₄.

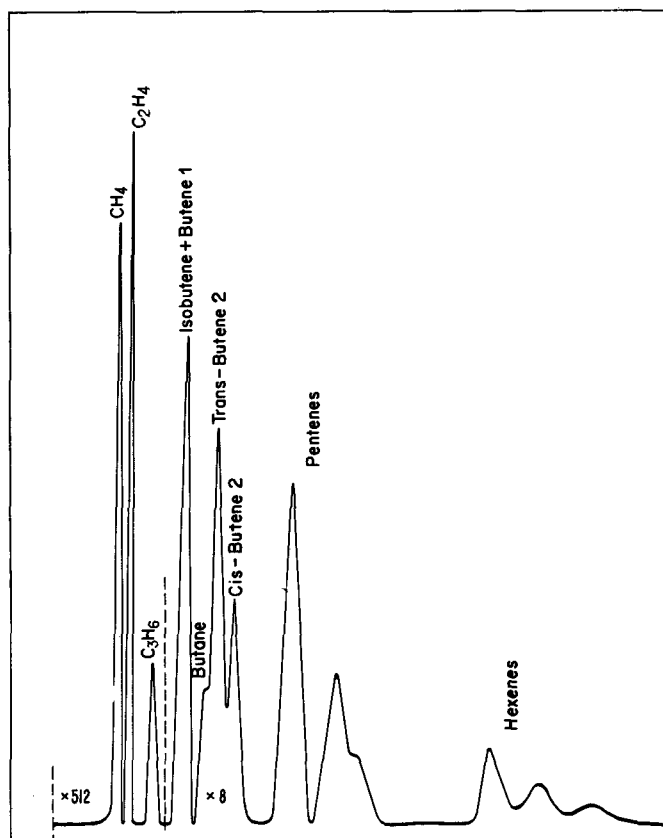


Fig. 4. Ethylammonium montmorillonite heated 720 hr at 220°C. Gas chromatographic analysis of the hydrocarbons in the gas phase.

Table 7. Hydrocarbon formation in sealed tubes at 240°C for 48 hr under a 30 mbar water pressure. The amounts are related to 1 g of the initial carbon contents and expressed with an arbitrary unit.

	MA-MT	EA-MT	TMA-MT	TEA-MT
C ₁	3.5	150	6	100
C ₂	19.5	756	5	480
C ₃	3	140	13.6	48
C ₄	2	151	156.5	1453
Total	28.0	1197	181.0	2081

Note. MA-MT—methylammonium montmorillonite; EA-MT—ethylammonium montmorillonite; TMA-MT—trimethylammonium montmorillonite; TEA-MT—triethylammonium montmorillonite.

hydrocarbons formed in the thermal process is higher for the pure chlorhydrate and still higher for the pure amine than for the clay organic complex, although the absolute reaction rate is always

weak. Therefore, the clay surface does not catalyze the formation of light hydrocarbons. The transalkylation processes are also observed for the chlorhydrates but they are far less advanced than in the thermal treatment of the alkylammonium montmorillonites.

Complementary experiments. For a better understanding of the mechanism of the observed reactions, some complementary experiments were performed, under a water pressure of 30 mbar. First, an ammonium montmorillonite was heated during 48 hr at 200°C, under a pressure of 1 bar of ethylene. Synthesis of small quantities of amines, with ethylamine and diethylamine the most apparent among them, is obvious (see Fig. 5B) after an examination of the products of desorption by the cobaltihexammine chloride. Then, ammonium and ethylammonium montmorillonites were heated for 48 hr at 200°C under a pressure of 1 bar of ethanol. With ethylammonium montmorillonite, the formation of ethylene and of ethylether can be

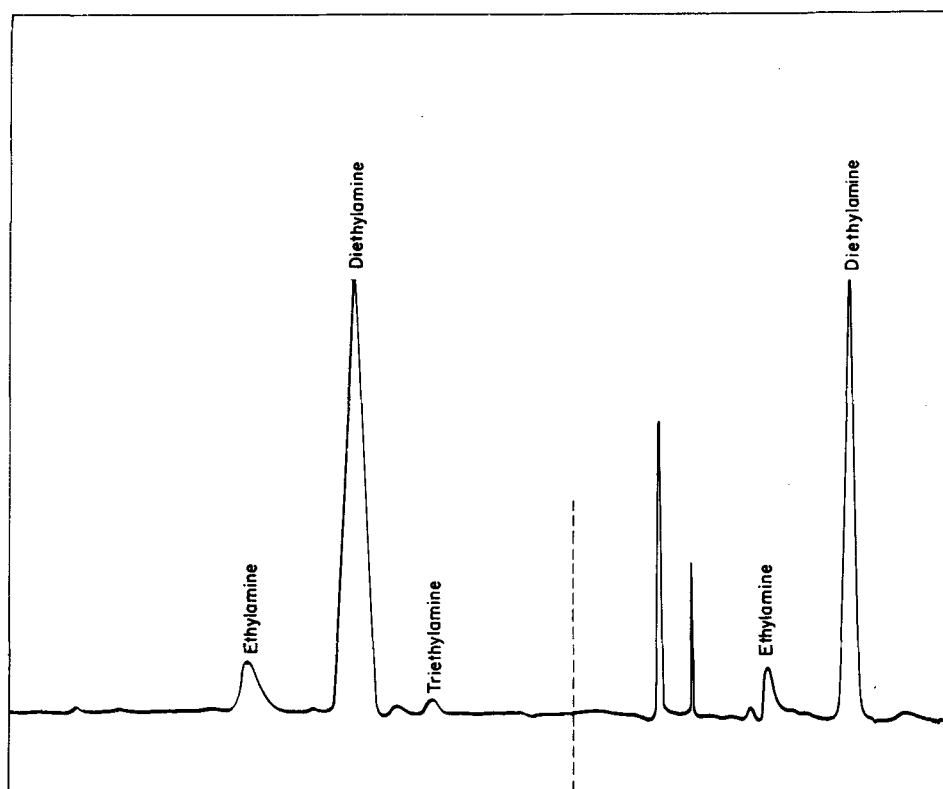


Fig. 5. *Left.* Ethylammonium montmorillonite heated 240 hr at 200°C under a pressure of 30 mbar of water. *Right.* Ammonium montmorillonite heated 48 hr at 200°C under a pressure of 1 bar of ethylene, and a pressure of 30 mbar of water.

seen by an examination of the gas phase after the experiment; an acceleration of the transalkylation process is noticeable, when compared with an ethylammonium montmorillonite heated under an inert atmosphere in the same conditions. With ammonium montmorillonite, ethylene and ethyl-ether are also formed; amines are synthesised, the most important being diethylamine, then ethylamine (see Figs. 6 and 7).

We must note here the results showing the formation of ethanol with ethylammonium montmorillonite heated with large excess of water.

DISCUSSION

The experimental results show that the reactions in an inert atmosphere on the montmorillonite surface consist mainly of transalkylation reactions. Derrien and Jungers (1962) and Catry and Jungers (1964) have observed similar reactions for *n*-butylamines on alumina at a higher temperature.

Other reactions may have varying degrees of

importance depending on the nature of the cation and on the experimental conditions, i.e. the formation of hydrocarbons (especially in the case of tetraethylammonium montmorillonite), hydrolysis reactions (under a higher water pressure) and the formation of unextractable products.

The hydration state of the clay has a considerable effect on the rate and on the nature of these reactions. Under the water pressure normally used, i.e. 30 mbar, the amount of water remaining in the clay surfaces is quite small. These residual water molecules are highly dissociated (Mortland *et al.*, 1963) and, accordingly, the proton mobility in the water adsorbed layer is very high (Hecht *et al.*, 1966).

Fripiat *et al.* (1965) and Touillaux *et al.* (1968) have estimated that the concentration of protons corresponding to the first monolayer of adsorbed water is considerably higher at room temperature than in ordinary liquid water.

Many examples of chemical reactions initiated

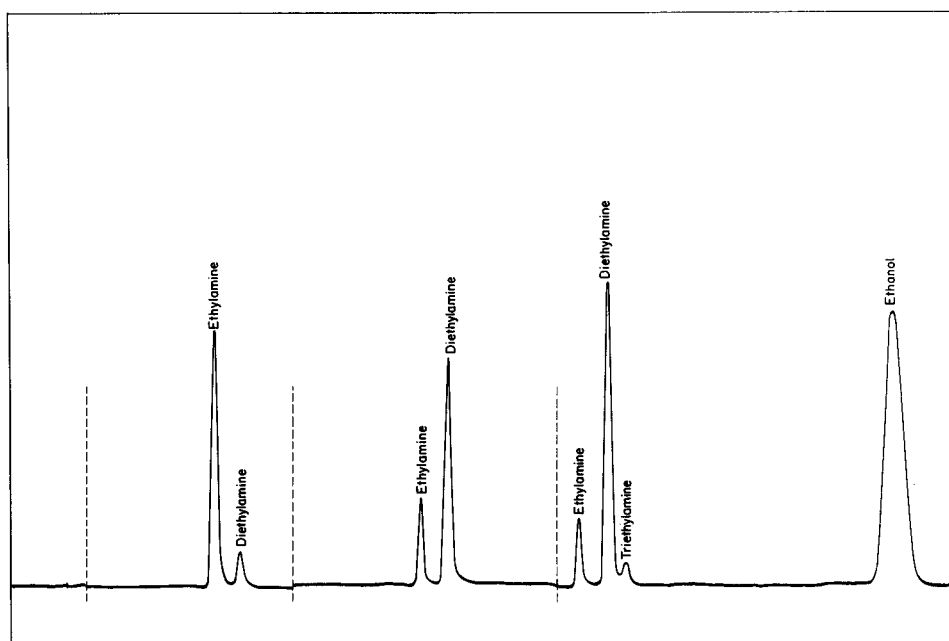
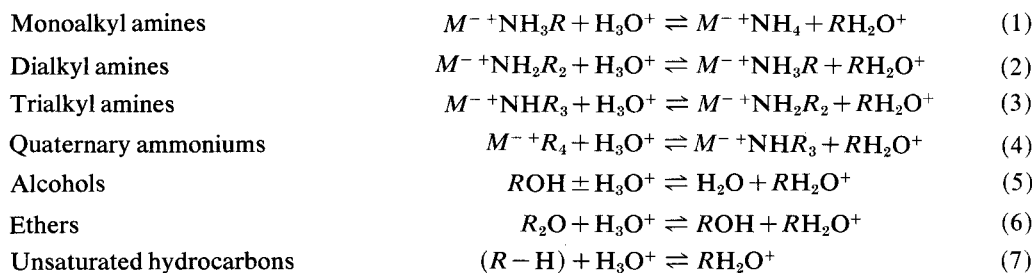


Fig. 6. Comparison between ethylammonium montmorillonite heated 48 hr at 200°C in different conditions. From left to right, without water; under a pressure of water of 30 m.b.; under a pressure of water of 30 m.b. and a pressure of ethanol of 1 bar.

by this high degree of surface acidity have been given by different authors, including: the formation of triphenylcarbonium from triphenylcarbinol (Fripiat *et al.*, 1964), the decomposition of amines in presence of oxygen (Calvet and Chaussidon, 1964), the polymerization of amino-acids (Cloos *et al.*, 1966, Fripiat *et al.*, 1966). Consequently the following reaction mechanism for the observed transalkylation processes may be suggested: The proton, or in a more realistic way the hydronium ion, since reactions occur in presence of water, interacts with alkyl chains to give an "activated" species, namely an oxonium ion; symbolizing the negative surface of the montmorillonite by M^- and the alkyl chain by R , the sequence of reactions may be written.

These reactions can, of course, proceed in both directions according to the thermodynamic and/or kinetic constants and the concentrations of the reactants; the main features of the experimental results may then be explained:

(1) Transalkylation with mono-, di-, tri-alkylamines: reactions (1) left to right followed by (2) right to left, (2) left to right followed by (3) right to left, (3) left to right followed by (4) right to left. (1) (2), (2) (3), (3) (1) form three couples of reactions related respectively to the transformation of mono-, di-, trialkylamines. Such a couple does not exist for ammonium and quaternary ammonium compounds. For the couple (1, 2), a calculation of the kinetics can be made with the values given by Table 4, in the case of ethyl radical; the overall



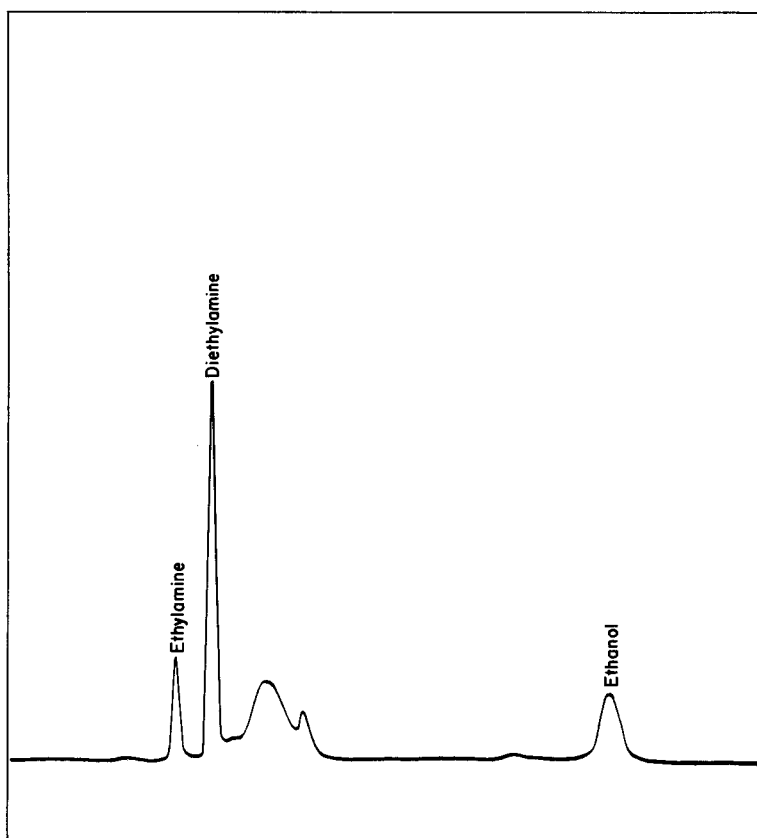


Fig. 7. Ammonium montmorillonite heated 48 hr at 200°C under a pressure of 30 m.b. of water and a pressure of 1 bar of ethanol.

reactions being written:



For this reaction from left to right, the apparent order is 2, and the activation energy found is 38 kcal/mole (see Fig. 8).

(2) Transalkylation with alcohols, ethers and unsaturated hydrocarbons: respectively reactions (5)–(7) proceeding from left to right followed by reactions of the group (1) (4) proceeding from right to left.

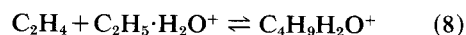
(3) Production of alcohol, with the organoclay complex exposed to a reasonably high water vapor pressure: then the reaction (5), following either of the (1)–(4) reactions, is favored in the direction left from right.

(4) Production of unsaturated hydrocarbons: reactions (1)–(6) proceeding from left to right, followed by reaction (7) proceeding from right to

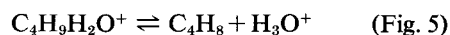
left. This reaction is generally (see hereafter) unimportant, being favoured only by high concentrations of RH_2O^+ , and is impossible when R is a methyl group (see examination of methylammonium montmorillonites).

(5) Higher rates of unsaturated hydrocarbon formation with quaternary ammoniums: in this case, there is no possible further transalkylation process, so RH_2O^+ becomes available for other reactions, the most important of them with a low water vapor pressure being reaction (7) from right to left.

(6) Polymerization: with unsaturated hydrocarbons may still occur another type of reaction, for instance for ethylene and ethylamines:



generally followed by:



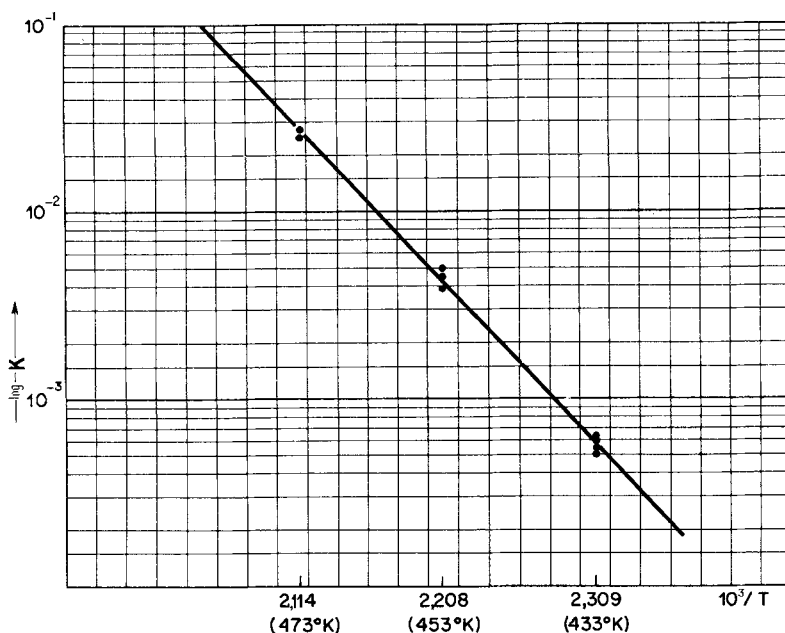


Fig. 8. Kinetics of transalkylation from ethylammonium. $2C_2H_5^+NH_3 \rightarrow (C_2H_5)_2^+NH_2 + ^+NH_4$, $\log K = \log A - E = 4.6 \times 1/T$.

In some cases concentration of this polymerized activated species may be sufficient to lead to heavy amines or may be heavy alcohols. Such heavy products would be very difficult to desorb from the clay surface.

(7) Inhibition of the whole sequence of reactions by the absence, or by a too large excess of water: in the first case, there is no more water available to give protons; in the second case, the proton concentration (acidity) is too low to make possible the reactions.

The thermal transformation of alkylammonium montmorillonite in an inert atmosphere reveals differences, as compared with the corresponding transformation in presence of oxygen as studied by Calvet *et al.* (1964). Several experiments carried out in presence of air, have confirmed the results reported by Calvet and Chaussidon, i.e. a faster increase of the NH_4^+ content. Transalkylation processes do not operate in this case, but a band appears at 1725 cm^{-1} which can probably be assigned to carbonyl groups. The high reactivity, and here especially the oxidability of the intermediate oxonium ion may explain these differences.

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Résumé— On a étudié la transformation thermique, dans des conditions d'hydratation variées, de cations alkylammonium adsorbés sur la surface d'une montmorillonite. Les conditions expérimentales ont été les suivantes: atmosphère inerte, températures inférieures à 250°C et durée de l'expérience allant jusqu'à 270 jours. Les réactions observées sont essentiellement des transalkylations pour lesquelles on propose un mécanisme de catalyse acide. Un haut degré de dissociation de l'eau restant sur la surface de l'argile est nécessaire et il est atteint pour des minéraux dont la teneur en eau optimale est assez basse.

Kurzreferat— Es wurde eine Untersuchung der thermischen Umwandlung von Alkylammonium Kationen, die unter verschiedenen Hydratationsbedingungen an der Oberfläche eines Montmorillonits adsorbiert waren, durchgeführt. Die Versuchsbedingungen waren: inerte Atmosphäre, Temperaturen unterhalb 250°C und Zeiträume von bis zu 270 Tagen. Die beobachteten Reaktionen waren in erster Linie Transalkylierungen für welche ein Mechanismus einer Säurekatalyse vorgeschlagen wird. Ein hohes Mass an Dissoziation des auf der Tonoberfläche verbleibenden Wassers ist erforderlich und wird für einen optimalen, und eher niedrigen Wassergehalt des Tones erreicht.

Резюме— Проведено изучение преобразования при нагревании алкиламмонийных катионов, адсорбированных на поверхности монтмориллонита различной степени гидратации. Условия эксперимента были следующими: инертная атмосфера, температура ниже 250°C, промежутки времени до 270 дней. Наблюдаемые реакции представляли, главным образом, трансалкиляцию; для них предложен механизм кислотного катализа. Высокая степень диссоциации воды, остающейся на поверхности глины, является необходимой и достигается при оптимальном и довольно низком содержании воды в глине.