KINETICS OF DECOMPOSITION OF COBALT COORDINATION COMPLEXES ON MONTMORILLONITE SURFACES

by

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ABSTRACT

Montmorillonite may adsorb cobalt(III)hexammine and cobalt(III)chloropentammine cations, and the C.E.C. determined for these complex cations is of the order of magnitude of that obtained with ammonium. The infrared spectra of these coordination complexes adsorbed by the clay are similar to those observed for the corresponding chloride salts. However, when montmorillonite treated with these coordination complexes is dehydrated in vacuum or under moderate temperature conditions ($<100°C$) in a dry atmosphere, the infrared spectra are deeply modified. The complex cations decompose with NH_3 evolution and ammonium formation. Cobalt(II)hydroxide is produced and ammonium cations balance the lattice electrical charge. The true decomposition rate was followed by IR absorbance of NH_4 which showed that the complex decomposition followed that for the homothetic decomposition of solid particles. The apparent activation energy of the decomposition was 20.5 and 43 kcal/mole for the $\{CoCl(NH_3)_5\}^{2+}$- and $\{Co(NH_3)_6\}^{3+}$-montmorillonite complexes respectively. An analysis of the combined chemical and IR data on the hexammine complex permitted calculation of the NH_3 diffusion rate between collapsed montmorillonite sheets. When the interplanar gap approaches $1Å$ the diffusion coefficient is approximately 7×10^{-19} cm²/sec. In contradiction to their stability in solutions, the cobalt(III)hexammine cation is less stable than the cobalt(III)chloropentammine cation when absorbed on montmorillonite.

INTRODUCTION

The cation exchange of montmorillonite with cobalt (III) hexammine chloride solutions has been studied by Morel (1957) and by Mantin and Glaeser (1960). The exchange of mono- or divalent ions by this complex cation has been proposed for rapid colorimetric determination of cation exchange capacity (C.E.C.). Helsen (1966) has measured the adsorption isotherms for the cation pairs $Na^+/Co(NH_3)_6^{3+}$, $Ca^{2+}/Co(NH_3)_6^{3+}$, and $Ce^{3+}/Co(NH_3)_6^{3+}$ on montmorillonite: the equilibrium constant for the $Ce^{3+}/Co(NH_3)_6^{3+}$-clay system was found to be equal to 2.2×10^{-4} at 25°C; the selectivity of montmorillonite for the coordination complex is thus very high even in the presence of another trivalent cation.

Cations such as $Co(NH_3)_6^{3+}$ or $\{CoCl(NH_3)_5\}^{2+}$ adsorbed on montmorillonite are easily detected by infrared spectroscopy: the strong NH_3 symmetrical deformation vibration doublet, which appears in gaseous ammonia

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at 931.6–968.1 cm^{-1} is shifted toward higher frequencies in coordination complexes as shown in Table 1.

If oriented clay films, suitable for spectral investigations, are brought into vacuum at room temperature or dried in the atmosphere at about 100°C, a rapid transformation of the infrared spectra is observed (Chaussidon, Calvet, Helsen, and Fripiat, 1963). The $Co(NH_3)_6^{3+}$ adsorbed on the clay decomposes as indicated by the increasing intensity of the deformation band of ammonium at 1432 cm^{-1}. The cation $\{CoCl(NH_3)_5\}^{2+}$ behaves similarly although the decomposition reaction is slower under similar conditions. This transformation was interpreted to be a consequence of the acid properties of residual water molecules left on the clay surface in vacuum or after heating at moderate temperature.
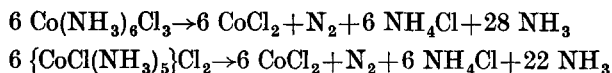
Mortland, Fripiat, Chaussidon, and Uytterhoeven (1963) have shown that NH_3 chemisorbed on montmorillonites saturated by mono- or divalent cations was completely converted into NH_4^+. This reaction was interpreted as follows:

$$M^{z+}(H_2O)+NH_3 \rightarrow (M-OH)^{(z-1)+}+NH_4^+$$
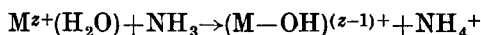
where M^{z+} represents the cation adsorbed on the clay. The dissociation degree of residual water molecules on Na- and Ca-montmorillonites was estimated by Fripiat, Jelli, Poncelet, and André (1965) to be in the order of magnitude of 10^{-2}, i.e. 10^6 times higher than in the liquid at the same temperature. This tremendous increase is believed to result from strong surface electrical fields. Thus, the decomposition process of cobalt coordination complexes on clay surface may be interpreted as an acid catalyzed reaction. The kinetics of such decomposition reactions are therefore relevant to the broad domain of surface activity.

It is interesting to point out that Cloos and Mortland (1965) have shown by infrared and X-ray diffraction that in a completely anhydrous medium, the physical adsorption of ammonia at −33°C by a cobalt(II)-saturated montmorillonite results in the formation of an octahedral coordination complex. The reactions studied here seem to be reversible to some extent in absence of water.

The decomposition of crystalline $Co(NH_3)_6Cl_3$ and $\{CoCl(NH_3)_5\}Cl_2$ has been studied by Wendlandt et al. (1963). D.T.A. shows a decomposition starting at about 200°C for cobalt(III)hexammine, and at about 250°C for cobalt(III)chloropentammine chlorides. In a helium flux, the proposed reactions are as follows (Wendlandt and Bear, 1961; Wendlandt, 1963):

$$6\ Co(NH_3)_6Cl_3 \rightarrow 6\ CoCl_2+N_2+6\ NH_4Cl+28\ NH_3$$
$$6\ \{CoCl(NH_3)_5\}Cl_2 \rightarrow 6\ CoCl_2+N_2+6\ NH_4Cl+22\ NH_3$$

The activation energy for the latter is about 28 kcal mole^{-1} (Wendlandt and Smith, 1963).

In solutions, $Co(NH_3)_6^{3+}$ is stable. However, in presence of silica gel, carbon black or Raney nickel, the rate of decomposition becomes noticeable

even at low temperature (Basolo and Pearson, 1958; Bjerrum, 1941). The complex $\{CoCl(NH_3)_5\}^{2+}$ is less stable and decomposes spontaneously and slowly at room temperature (Bjerrum, 1941; Watkins and Jones, 1964). However both complexes are stable enough to permit the exchange reaction with montmorillonite to occur at room temperature without noticeable hydrolysis.

PROCEDURES

Clay Samples

Montmorillonite from Camp-Berteau (Morocco) was saturated with NaCl and the $<2\mu$ fraction was separated by centrifugation (Léonard, Servais and Fripiat, 1962). The clay-suspensions (1%) were saturated in cobalt complexes with 0.5 N solutions of $Co(NH_3)_6Cl_3$ or $\{CoCl(NH_3)_5\}Cl_2$.

Films of $Co(NH_3)_6^{3+}$- or $\{CoCl(NH_3)_5\}^{2+}$-clays are easily prepared when the suspension is allowed to dry slowly at room temperature under a relative humidity of 70%.

Chemical Analysis

NH_3, NH_4^+ and the contents in cobalt complexes were determined by microdistillation, Cl^- by Volhardt titration and N_2 by gas volumetry.

$Co(NH_3)_6Cl_3$ and $\{CoCl(NH_3)_5\}Cl_2$ were commercial products (Hopkins & Williams) of the right composition.

Infrared Spectroscopy

For infrared kinetic studies, a cell was designed to permit the sample to be heated at controlled temperature in an air flux of constant relative humidity (50%) at 30°C. The sample holder was heated at the desired temperature before introducing the clay film. The spectra were then recorded continuously between 8 and 6.5μ with a double beam Beckman IR4 fitted with CaF_2 optics.

The kinetic study from chemical data was performed using an oven having about the same characteristics as the IR-cell, but the films were introduced into small cylindrical pyrex pans which could be dropped in the distillation apparatus for NH_3 determination.

X-ray Diffraction

A Philips diffractometer equipped with a copper tube was fitted with a sample holder which could be maintained at constant temperature up to 300°C.

EXPERIMENTAL RESULTS

Stoichiometry

The stoichiometry of the reactions was studied by analyzing the solid and the gas phases after complete decomposition under severe temperature conditions. For $Co(NH_3)_6^{3+}$-montmorillonite, at 110°C and after approximately 70 min, the ratio of the residual NH_4^+ content to the initial NH_3 content was equal to 0.51 ± 0.01, while at 200°C, after 4 hr, this ratio decreased to 0.46. Under these conditions, some decomposition of NH_4^+ adsorbed by the clay occurs. A simultaneous analysis of the gas phase showed that after complete decomposition, 47.5% of initial NH_3 was recovered and this gas phase contained 2.7 ± 0.8 moles of N_2 per 100 moles of NH_3. The small volumes of N_2 evolved account for the low accuracy of these determinations. The stoichiometry of the decomposition reaction was then written as follows:

$$6\{Co(NH_3)_6^{3+}\}_{ads} + 12H_2O \rightarrow 6\{Co(OH)_2\}_{ads} + 18\{NH_4\}_{ads} + 16NH_3 + N_2 \quad (a)$$
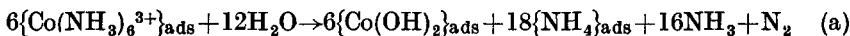
Cobalt(II)hydroxide could not be removed except by acid leaching. After complete decomposition, no trace of iodine could be detected by treating the clay with an acid potassium iodide solution; this indicated that the reduction of Co^{3+} to Co^{2+} was complete.

For the montmorillonite samples saturated in $\{CoCl(NH_3)_5\}^{2+}$ the residual chloride content was determined after complete decomposition and was found equal to the initial concentration within the experimental error. The NH_4^+ content approximated the C.E.C. value of montmorillonite. The gas phase was also a mixture of NH_3 and N_2, the ratio N_2/NH_3 (in moles per cent) being 2.6 ± 0.9. Titration by KI solutions, as above, indicated again a complete reduction of Co^{3+} to Co^{2+}. The decomposition of the adsorbed cobalt(III)chloropentammine cation was represented as follows:

$$6\{CoCl(NH_3)_5\}_{ads}^{2+} + 6\,H_2O \rightarrow 12\{(NH_4)\}_{ads} + 3\,CoCl_2 \\ + 3\,Co(OH)_2 + 16\,NH_3 + N_2 \quad (b)$$
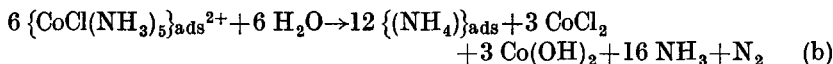
X-ray Diffraction

The 001 reflections of both air-dried $Co(NH_3)_6^{3+}$ and — $\{Co\,Cl\,(NH_3)_5\}^{2+}$ montmorillonites are rational and from the four first orders, the basal distance was found to be 14.5 ± 0.2 Å. This spacing is in good agreement with the calculated value $(9.6 + 5)$ Å, allowing 5 Å to the cation diameter and 9.6 Å to the thickness of the silicate sheet.

After complete decomposition at 170–200°C, the 001 reflection shifted to 10.4 Å for the montmorillonite initially saturated in $Co(NH_3)_6^{3+}$. Under the same conditions, the 001 reflection of montmorillonite initially saturated by cobalt(III)chloropentammine remained at a slightly higher value (10.8 Å). Figure 1 shows the shift of the reflection in the course of decomposition.
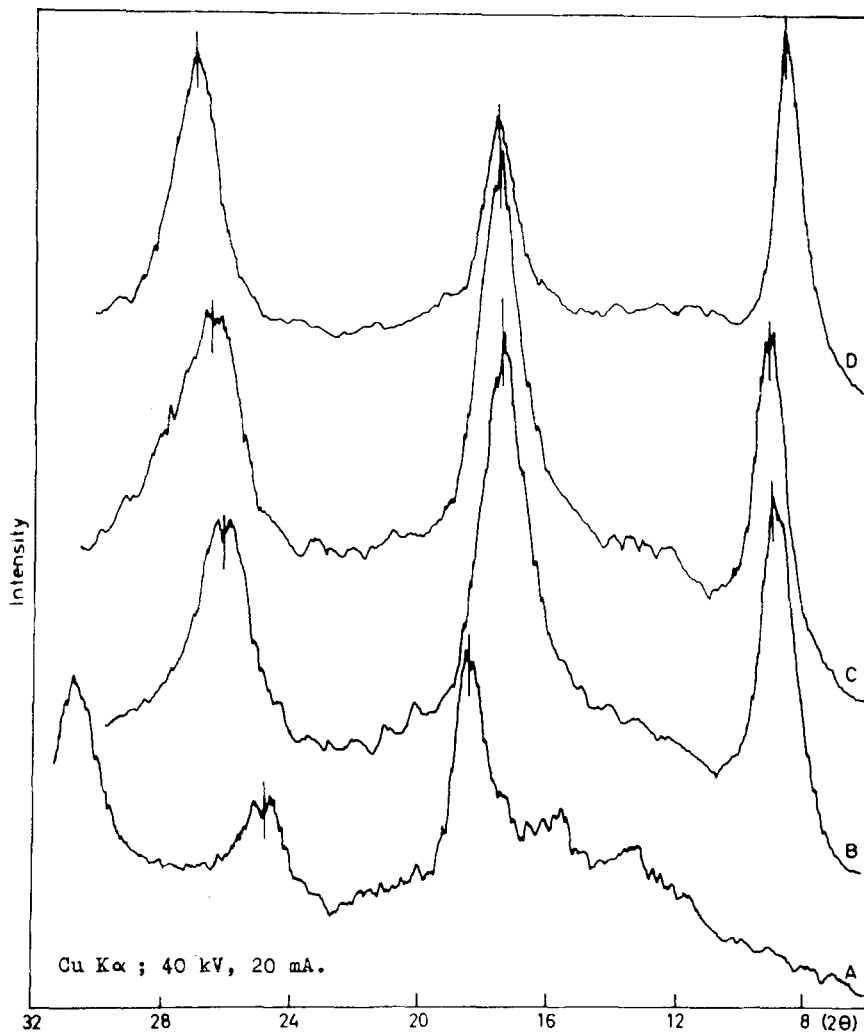
Cu Kα ; 40 kV, 20 mA.

FIG. 1. X-ray diffraction patterns of oriented cobalt(III)hexammine saturated montmorillonite films during heating: A: room temperature; B: 100°C (under vacuum); C: 300°C (under vacuum); D: 300°C (in air).

Infrared Spectroscopy

Some examples of characteristic infrared spectra are shown in Figs. 2 and 3. After decomposition, the marked change in the 1430 cm^{-1} region is clearly observed, as well as the disappearance of the band in the $1370–1300$ cm^{-1} region. The relationships between the complexes and the absorption bands
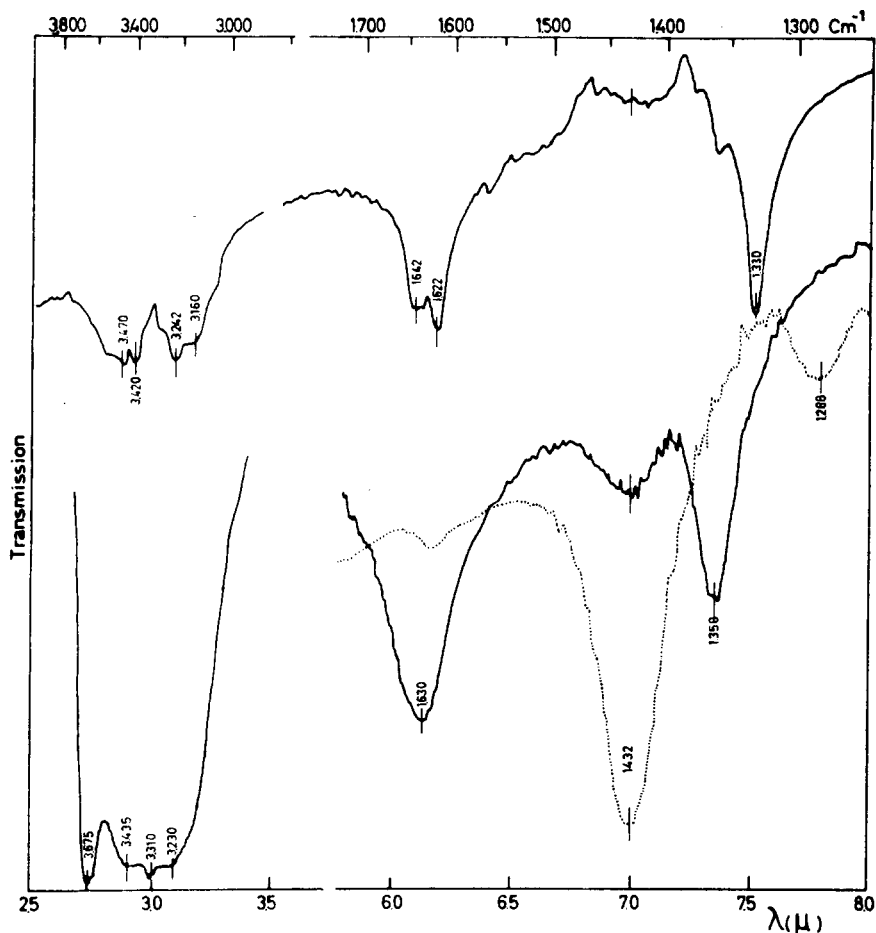
FIG. 2. IR absorption spectra of films of $Co(NH_3)_6^{3+}$-montmorillonite. From above: reference spectrum of pure cobalt(III)hexammine chloride dispersed in KBr (concentration 5‰); $Co(NH_3)_6^{3+}$-montmorillonite before decomposition of the complex (air dry film) and after complete decomposition (remark the strong NH_4^+-band at 1432 cm^{-1}).

are indicated in Table 1. The strong band at 3675 cm^{-1} is the OH stretching vibration of the clay. The diffuse band at 1630 cm^{-1}, due to the deformation vibration of water molecules, overlaps with the NH_3 asymmetrical deformation.

The shift of the NH_3 symmetrical deformation band for both adsorbed complexes with respect to their chloride salts is of the order of magnitude of 28 ± 3 cm^{-1} towards higher frequency. This is probably due to the hydrogen bonding of NH_3 with hydration water molecules still present.
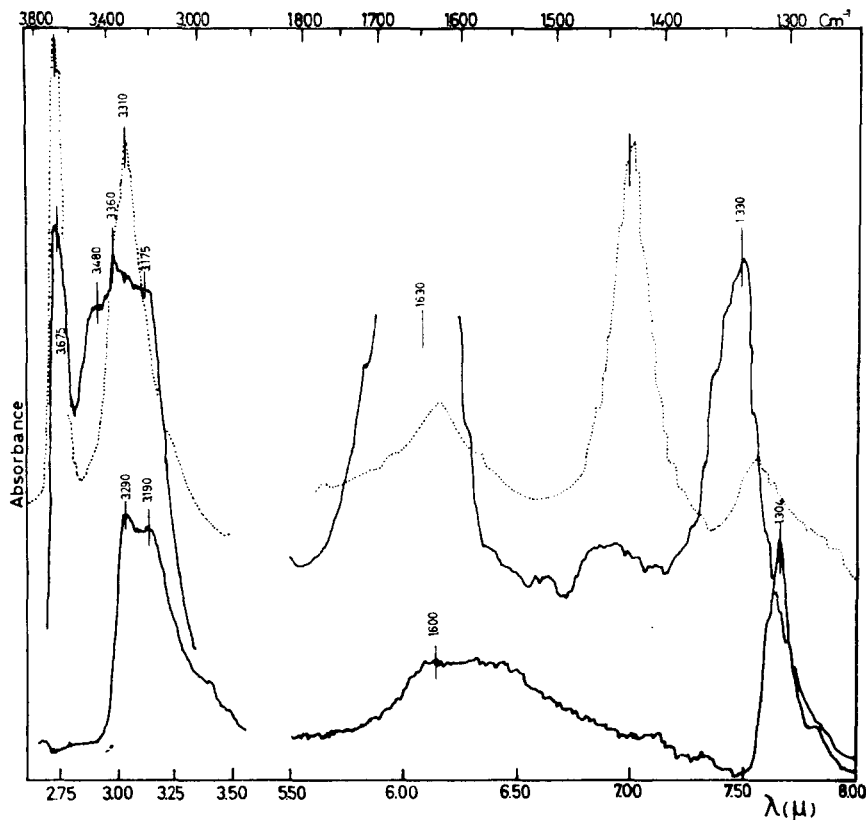
FIG. 3. IR absorption spectra of films of $CoCl(NH_3)_5^{2+}$-montmorillonite. From below: reference spectrum of pure chlorocobalt(III)pentammine-chloride dispersed in KBr (concentration 5‰); $CoCl(NH_3)_5^{2+}$-montmorillonite before decomposition of the complex (film dried in an atmosphere of 70% humidity) and after decomposition of the complex (note the strong band at 1432 cm⁻¹).

During the decomposition reaction, the absorbance of the 1432 cm⁻¹ band increased progressively while the intensity of the NH_3 symmetrical deformation (at 1358 cm⁻¹ for $Co(NH_3)_6^{3+}$ and at 1330 cm⁻¹ for $\{CoCl(NH_3)_5\}^{2+}$) decreased as shown in Fig. 4.

The continuous change in the 1432 cm⁻¹ absorbance band therefore may be used for determining the progression degree (a) of the decomposition reaction with respect to the time t. The progression degree (a) is measured by the ratio of the NH_4-content at the time t to the NH_4-content after complete decomposition, and is thus equal to the ratio of the NH_4 absorbance (at 1430 cm⁻¹) measured in the course of the reaction and after complete decomposition.
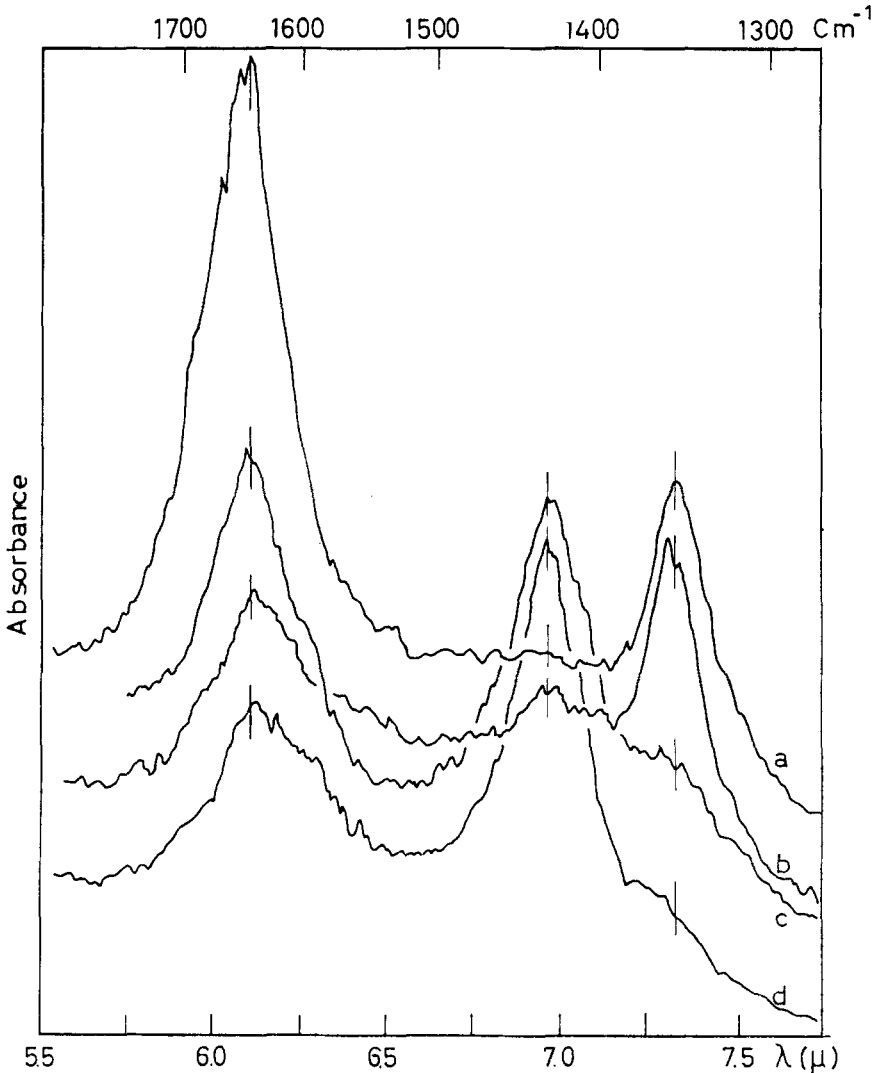
FIG. 4. IR spectra of $Co(NH_3)_6^{3+}$-montmorillonite at 59°C as function of time. a, b, c, and d after 0, 3, 24, and 100 min respectively.

When a was plotted with respect to t, smooth curved functions, concave towards the abcissa, were obtained. From these functions the time $t_{0.9}$ or $t_{0.5}$ necessary to perform either 90% or 50% of the decomposition were determined, and the reduced times $t/t_{0.9}$ or $t/t_{0.5}$ were calculated (by chemical means a never reaches 0.9). The kinetic process then was exposed better in

TABLE 1.—OBSERVED INFRARED ABSORPTION FREQUENCIES OF THE COBALT(III)
COMPLEXES AND OF THE RELATED COMPOUNDS

	NH as. str.*	NH s. str.*	NH_3 as. def.*	NH_3 s. def.*
$Co(NH_3)_6Cl_3$ (in KBr) (a, b)	3470 (2430)	3242	1642	1330
$Co(NH_3)_6{}^{3+}$-Mont.	3435	3230	1630	1358
$\{CoCl(NH_3)_5\}Cl_2$ (in KBr) (c)	3290	3190	1600	1304
$CoCl(NH_3)_5{}^{2+}$ Mont.	2480	3175		1330
NH_4 Mont.	3310			1432
NH_4Cl	3138	3041	1710	1403
NH_3 (gaseous) (a)	3414	3337	1628	932
H_2O (liquid) (a)	3445	3219	1627	968

* *Legend* as. str. asymmetrical stretching, s.str. symmetrical stretching,
  as. def. asymmetrical deformation, s. deg. symmetrical deformation.
  For the assignment of the absorption frequencies see (a) Nakamoto (1963)
  (b) Block (1959) (c) Shimanouchi and Nakagawa (1962).

terms of the reduced coordinates a $(t/t_{0.9})$ as shown in Fig. 5. The broken line represents the theoretical function calculated by Delmon (1961) for the homothetic decomposition of solid particles, characterized by a particle size distribution of the type represented in Fig. 5. The $t_{0.9}$ values used for determining $t/t_{0.9}$ are contained in Table 2. Taking into account the relative uncertainty of the absorbance determinations, the experimental data obtained for the decomposition of $Co(NH_3)_6{}^{3+}$ saturated montmorillonites fit reasonably well the theoretical curve, irrespective of the temperature conditions.

The data for $\{CoCl(NH_3)_5\}^{2+}$ saturated montmorillonites do not fit the same theoretical function presented in Fig. 5. No apparent reason was found to explain the discrepancy between the behaviours of these two complex cations.

The $t_{0.9}{}^{-1}$ as well as the $t_{0.5}{}^{-1}$ values may be considered as proportional to the reaction rate; consequently, the activation energy may be determined by plotting $\log t_{0.9}{}^{-1}$ or $\log t_{0.5}{}^{-1}$ against the reciprocal of the reaction temperature (T^{-1}) as shown in Fig. 6(a) and (b). The activation energy for the decomposition of $\{CoCl(NH_3)_5\}^{2+}$ saturated montmorillonite amounts to 20.5 kcal mole^{-1}. This value is noticeably lower than that (28 kcal mole^{-1}) obtained by Wendlandt and Smith (1963) for $\{CoCl(NH_3)_5\}Cl_2$ decomposition and unexpectedly lower than the value obtained for the cobalt(III)hexammine montmorillonite decomposition (43 kcal). Unfortunately, no reference data for $Co(NH_3)_6Cl_3$ were found.

Kinetics from Chemical Data

From the reaction stoichiometry the true progression degree (a) is determined from the spectroscopic data. If A_a means the amount of $NH_4{}^+$ formed
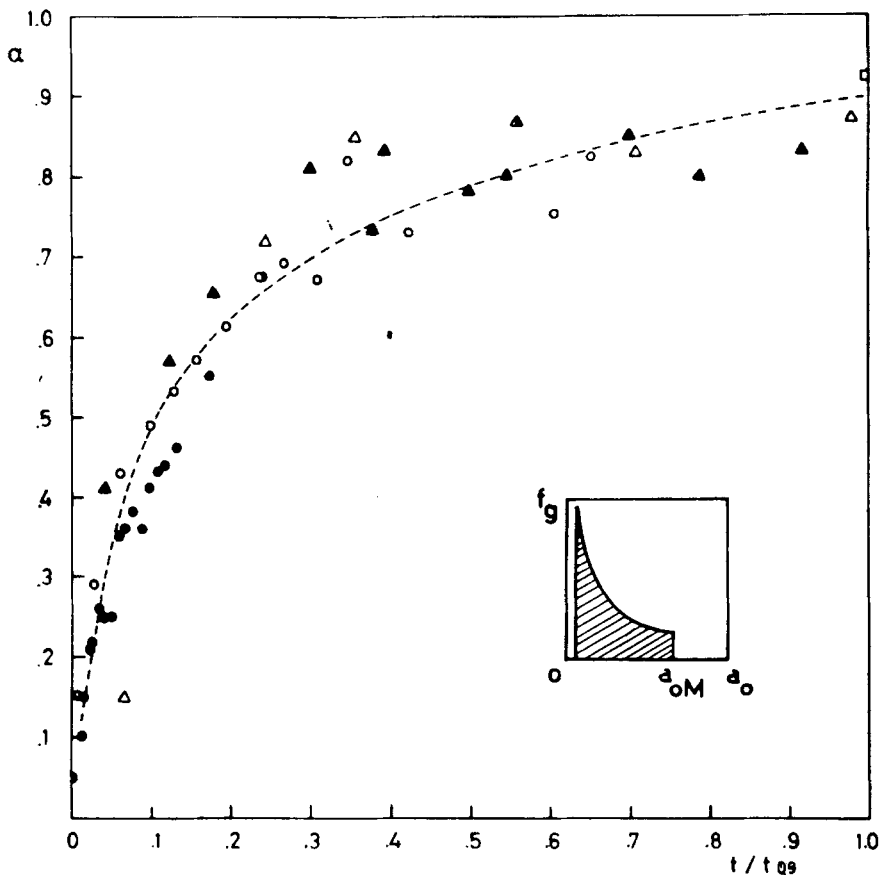
FIG. 5. Progression degree a (from spectroscopic data) for $Co(NH_3)_6{}^{3+}$ montmorillonite against the reduced time $t/t_{0.9}$ at different temperatures, ● 45°C; ○ 55°C; ▲ 59°C; ▲ 62°C; △ 65°C; □ 70°C. Dotted line: theoretical function calculated for the particles size distribution inserted.

after the time t and A_0 the initial NH_3 content:

$$a = \frac{2A_a}{A_0} \tag{1}$$

for the $Co(NH_3)_6{}^{3+}$ decomposition. For the $\{CoCl(NH_3)_5\}^{2+}$ decomposition the numerical factor 2 of relation (1) becomes 2.5. It is clear that for $a \rightarrow 1$, $A_a \rightarrow A_0/2$ in the first and $A_a \rightarrow A_0/2.5$ in the second case.

Considering the geometry of the system, and especially the interlamellar space, the true decomposition degree cannot be obtained from chemical data: $NH_4{}^+$ and NH_3 liberated from the complex cation decomposition are present and simultaneously detected by the chemical procedure.
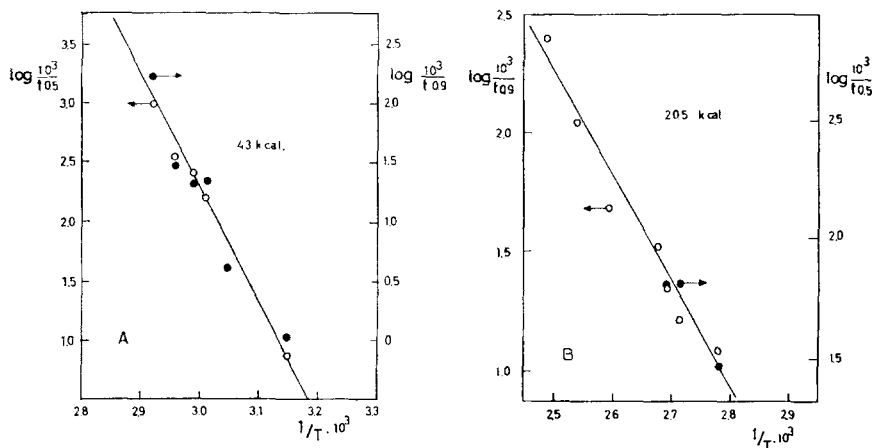
FIG. 6. Plots of $\log t_{0.5}^{-1}$ or $\log t_{0.9}^{-1}$ versus T^{-1} for $Co(NH_3)_6^{3+}$- and $CoCl(NH_3)_5^{2+}$-montmorillonites (A and B) respectively.

TABLE 2.—TIME VALUES CORRESPONDING TO A DECOMPOSITION DEGREE OF 0.5
FOR THE COBALT(III)COMPLEXES SATURATING MONTMORILLONITES

Samples	From chemical data		From spectroscopic data		
	$T°C$	$t_{0.5}$ (min)	$T°C$	$t_{0.5}$ (min)	$t_{0.9}$ (min)
$Co(NH_3)_6$-Mont.	85	90	45	920	
	71	130	55	250	
	69	220	59	45	38
	57	280	62	50	38
	65	345	65	33	34
			70	6	8
$CoCl(NH_3)_5$-Mont.	147	100	87	82	
	145	300	95	60	
			98	45	
			100	30	29
			112	21	22
			121	9	10
			128	4	3

The following relation between a and the advancement determined from from chemical data (a_{ch}) can be stated for $Co(NH_3)_6^{3+}$:

$$a = a_{ch} - \frac{2A_d}{A_0} \tag{2}$$

where A_d is the content in "free" NH_3 diffusing between the clay sheets.

As a matter of fact, the comparison of the plots a and a_{ch} versus t shows the latter to be always lower under the same temperature conditions.

The ratio A_d/A_0 can be calculated from a and a_{ch} obtained at the same temperature. From this ratio, which has no direct physical meaning, another function may be easily derived. This new function called f_{diff} represents the amount of free NH_3 molecules that have diffused:

$$f_{diff} = 1 - \frac{9}{4} \frac{A_d}{a A_0} = 1 - \frac{9}{8} \frac{a - a_{ch}}{a} \qquad (3)$$

When we apply this formula to the case of the decomposition of chloropentammine, the numerical factor 9/8 of equation (3) cancels in 15/16 according to reaction stoichiometry [see decomposition reaction (b)]: f_{diff} is plotted against t in Fig. 7(a) and (b).
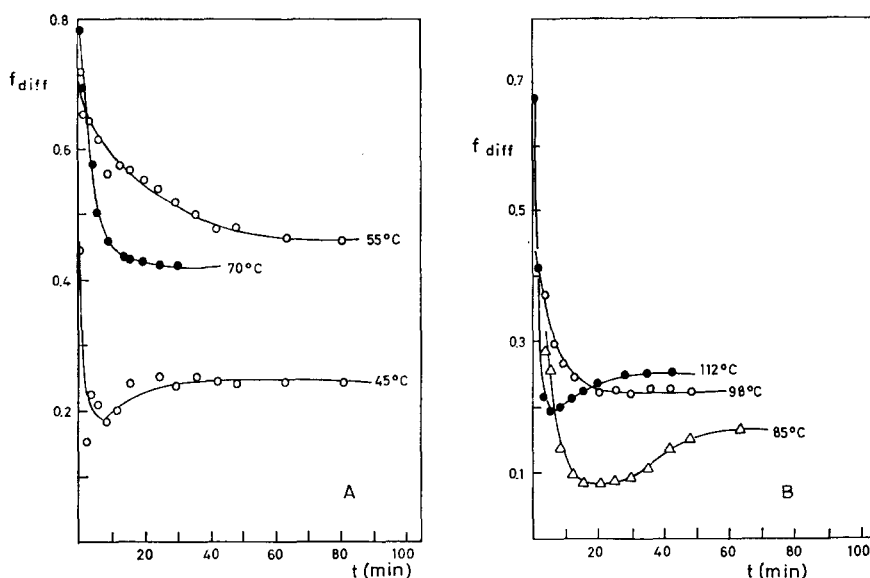

Fig. 7. f_{diff} plotted against time for $Co(NH_3)_6{}^{3+}$-(A) and $CoCl(NH_3)_5{}^{2+}$-(B) montmorillonites respectively.

It was observed that f_{diff} decreased very rapidly at the very beginning of the reaction and reached an approximately constant level after about 10–20 min. This may be interpreted by assuming a stationary diffusion process beyond this period of time. For disk-shaped platelets such as montmorillonite particles, the diffusion phenomenon must be symmetrical around the c-axis. Under these conditions, Jost (1960) has shown that the solution of Fick's second law:

$$\frac{\delta C}{\delta t} = D \left[\frac{\delta^2 C}{\delta r^2} + \frac{1}{r} \frac{\delta C}{\delta r} \right] \qquad (4)$$

is given by:

$$C(r, t) = 2C_0 \sum_{\nu = 1}^{\infty} \frac{1}{\xi_\nu J_1(\xi_\nu)} \, J_0 \, (\xi_\nu r/r_0) \exp \, (- \, \xi_\nu{}^2 \, Dt/r_0{}^2) \qquad (5)$$

where C is the surface concentration of diffusible species at the distance r from the center of the disk, D the diffusion coefficient and ξ_ν the root of the Bessel function J_2 of the νth order; C_2 is the uniform initial surface concentration and r_0 the disk radius. Eeckman and Laudelout (1961), who applied relationship (5) to the spontaneous "aluminization" of acid montmorillonites, have shown that it may be satisfactorily approximated by

$$\ln \gamma = 2 \ln \frac{2}{\xi_1} - \xi_1{}^2 \, \tau \qquad (6)$$

where $\gamma = C/C_0$ and $\tau = Dt/r_0{}^2$ and $\xi_1 = 2.405$ at rather high values of the time. Using our symbols and decimal logarithms, relationship (6) becomes:

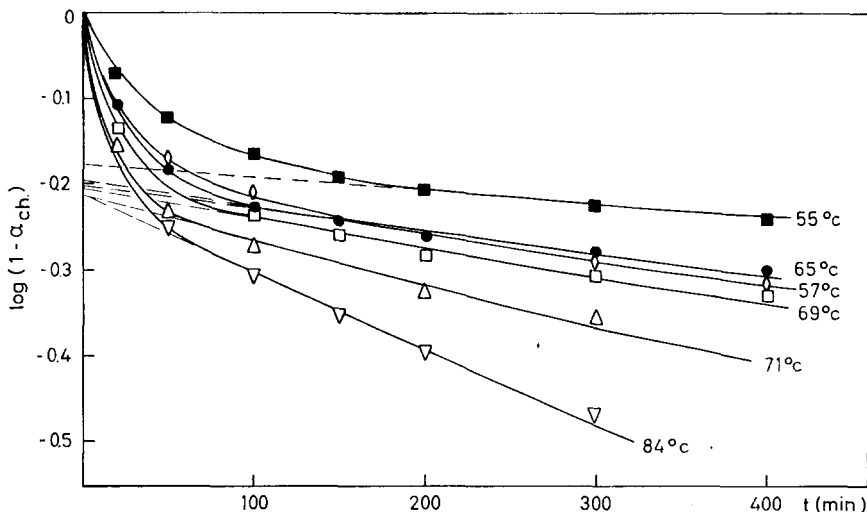$$\log \, (1 - a_{\text{ch}}) = - \, 0.16 - 2.515 \frac{D}{r_0{}^2} \, t \qquad (7)$$

FIG. 8. Log $(1 - a_{\text{ch}})$ as function of time for $Co(NH_3)_6{}^{2+}$-montmorillonite.

It may be observed by plotting log $(1 - a_{\text{ch}})$ against t (Fig. 8) that the experimental data obtained for $t > 75$ min fit reasonably well straight lines converging towards a common intercept at about -0.2 or -0.13 for the decompositions of $Co(NH_3)_6{}^{3+}$- and $\{CoCl(NH_3)_5\}^{2+}$-montmorillonites respectively. According to Eeckman and Laudelout (1961), the r_0 value for the Camp-Berteau montmorillonite is of the order of magnitude of 80Å.

The diffusion coefficients, obtained from the slope of the linear relationship, fit well the Arrhenius equation $D = D_0 \exp \, (- \, E/RT)$. From the plots

of log D against $1/T$, the activation energy E of the diffusion process has been calculated. Some examples are shown in Table 3.

TABLE 3.—DIFFUSION COEFFICIENTS AND ACTIVATION ENERGIES OF DIFFUSION FOR NH_3 BETWEEN MONTMORILLONITE SHEETS

	T (°K)	D (cm² sec⁻¹)	E (kcal mole⁻¹)
$Co(NH_3)_6$-Mont.	328	6.6×10^{-19}	13.7
$CoCl(NH_3)_5$-Mont.	385	9.4×10^{-19}	13.7

DISCUSSION

The progression of the decomposition process is exposed by a, obtained spectroscopically. The progression of the entire process, including the decomposition of the complex cation and the diffusion of NH_3, is expressed by a_{ch}, calculated from chemical data. The fraction of diffusing NH_3 molecules (f_{diff}) is derived from a and a_{ch} according to relationship (3). The model representing the initial situation for montmorillonites saturated in octahedral cations may be visualized as follows. The charge balancing cations are located either on the external surface or in the interlamellar space. Hydration water molecules are hydrogen bonded to each other and to NH_3 ligands. The frequency shift observed in Figs. 2 and 3, for the NH_3 symmetrical deformation vibration accounts for the formation of the N—H . . . O bond.

The water molecules left on montmorillonite surfaces after outgassing under vacuum at room temperature, or drying in the air at higher temperature, have an unusual degree of dissociation. It approximates 1% in the monolayer according to Fripiat, Jelli, Poncelet, and André (1965). At lower water contents, it probably increases still more because the proton contents of base-saturated montmorillonite outgassed at room temperature are high enough to transform triphenylcarbinol into triphenyl-carbonium (Fripiat, Helsen, and Vielvoye, 1964). It may therefore be assumed that an intermediate state like this:

$$
\begin{array}{ccc}
H^+ & & H \\
| & & | \\
H—O & \ldots\ldots\ldots & H—N—Co \\
| & & | \\
H & & H
\end{array}
$$
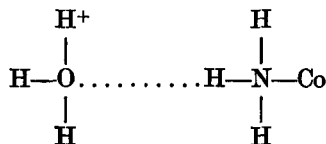
exists before the transfer of the proton on the nitrogen atom and the rupture of the Co—N bonds. The decomposition of the complex cation is provoked by proton transfer and probably occurs at once because, as shown in Fig. 4, no transient spectral feature which would support hypothetical transition structure has been observed. The broadening of the 6μ band and the shoulder

which appears at 1590 cm^{-1} during the decomposition is obviously due to NH$_3$ molecules still in the interlamellar space and diffusing outwards from the particles.

The relationship between the 001 spacing in randomly interstratified 10/14 Å mixed layers and the percentage P of collapsed interlamellar spaces has been calculated by MacEwan (Brown, 1961). This relation has been used to correlate P with the progress of the Co(NH$_3$)$_6$$^{3+}$ decomposition, expressed by a_{ch}. The experimental data fit well the straight line $a_{ch} = \frac{1}{2} P$ as shown in Fig. 9.
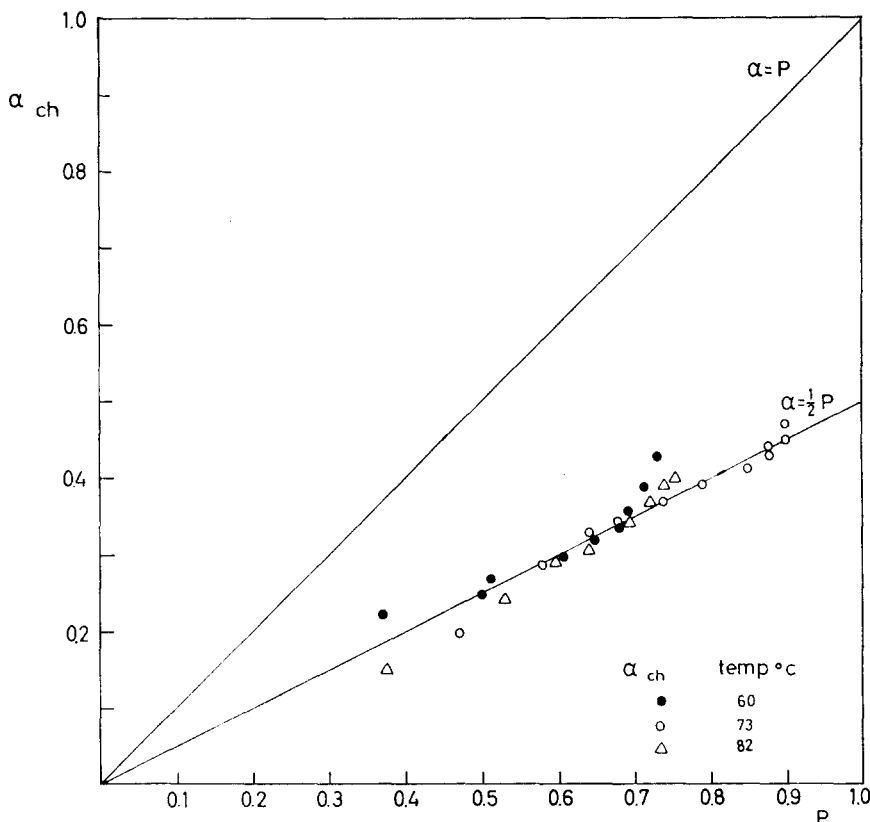

FIG. 9. a_{ch} versus P for Co(NH$_3$)$_6$$^{3+}$-montmorillonite. P: percentage collapsed clay sheets.

This agreement suggests that all the interlamellar spaces are already collapsed when one half of the NH$_3$ molecules which have to escape from the solid have been removed. Such a view supports the above conclusion that no intermediate complex is formed during the decomposition, because an eventual tetrahedral or coplanar cobalt complex would maintain a higher

transient rational spacing. Moreover, the decomposition, as observed from chemical data, is achieved at 50% only when all the sheets have collapsed. This also explains the rather low diffusion coefficient and the high activation energy obtained for NH_3 (Table 3).

The proposed decomposition mechanism is also in agreement with the model suggested by the best fitting of the "spectroscopic" α with the theoretical function calculated by Delmon (1961) for the homothetic decomposition of a solid. This may be visualized as follows: the decomposition occurs first for the complex cations adsorbed on external surface and then affects the species adsorbed between the sheets near the margin of the particles. The reaction interface progresses toward the center of the particles while the NH_3 molecules evolved in the course of the decomposition must travel outwards over longer distance before reaching external surface of the particles.

The latter remark is in agreement with the rapid decrease of the fraction of diffusing molecules f_{diff} with respect to the time at the beginning of the decomposition (Fig. 7(a) and (b)) since the diffusing species are moving at this moment in a free space. After the sheets have collapsed, f_{diff} reaches a constant value and all the NH_3 molecules diffusing at this time are characterized by the diffusion parameters contained in Table 3. In this regard, it is interesting to point out that the diffusion coefficients as well as the activation energies observed for NH_3 in the collapsed system are of the order of magnitude of those obtained by Eeckman and Laudelout (1961) for H^+/Al^{3+} interdiffusion on montmorillonite surfaces.

It is remarkable that the decomposition of $\{CoCl(NH_3)_5\}^{2+}$ saturated montmorillonite does not obey either the theoretical function calculated for the homothetic decomposition or the linear relationship $\alpha = \frac{1}{2} P$. There is a probable connection between these observations, but thus far the explanation has not been found.

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