

THE DECOMPOSITION OF ORGANIC AMINES ON MONTMORILLONITES UNDER AMBIENT CONDITIONS

(Received 2 April 1977; and in final form 26 April 1977)

INTRODUCTION

The physical and chemical interactions between organic amines and mineral surfaces are of considerable importance in many industrial applications. For example, the preparation of organophilic minerals often involves the adsorption of organic amines, or the ion exchange of the minerals with quaternary ammonium salts (Jordan, 1951; Miller and Faust, 1972). Chemical interactions occurring in these systems have been studied because of their relevance to an understanding of the chemical nature of the clay surface. A number of these studies have reported on the decomposition of adsorbed amines and alkylammonium-mineral complexes at elevated temperatures, usually in excess of 100°C (Chaussidon and Calvet, 1965; Weiss and Roloff, 1963; Durand, Pellet and Fripiat, 1972; Chou and McAtee, 1969). It is now well established that under these conditions the mineral may have potential strong-acidity, and these reactions have been explained in terms of acid-induced decomposition or rearrangement of the adsorbed amines or their derivatives. However, there have been few studies of the reactions of organo-mineral complexes at temperatures below 100°C, under conditions where retention of adsorbed water could be expected to moderate the mineral surface acidity.

In this study, we report on the decomposition of exchangeable quaternary ammonium ions on montmorillonite surfaces under such carefully chosen mild conditions.

EXPERIMENTAL

Five Wyoming montmorillonites supplied by Georgia Kaolin were used: commercially available Volcay XX; Al³⁺-exchanged, and Fe³⁺-exchanged Volclays prepared using standard procedures; and two samples from the Mowry formation, Kaycee. The latter two samples were differentiated, respectively, by their superficial blue or yellow coloration.

Cetyltrimethylammonium bromide (CTAB), from British Drug Houses Ltd, consisting essentially of hexadecyltrimethylammonium bromide plus small amounts of homologous alkyltrimethylammonium bromides, was used as received.

Aqueous suspensions of the montmorillonites (5% solids) were treated with solutions of CTAB in amounts equivalent to 50, or to 100% of the exchange capacity of the montmorillonites. The resultant mixtures were stirred at 20° for 15 hr, then filtered and the organomontmorillonites washed on the filter until the filtrates were bromide-free. The solids were then dried in air at 20°, the air-dry products sealed in glass vessels under N₂ or O₂ atmospheres and then stored at ambient temperature (19–20°) for periods of up to 5 months.

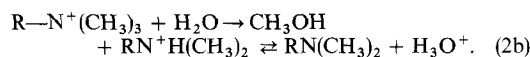
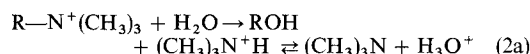
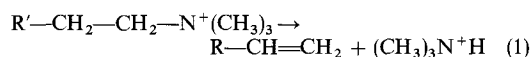
After storage, the head-space vapors were first sampled, and then the organominerals extracted with CHCl₃. The vapors and extracts were analysed using a Finigan 3300 gas-chromatograph-mass spectrometer equipped with a SE-30 SCOT column.

RESULTS AND DISCUSSION

Cetyltrimethylammonium bromide was chosen as a convenient model for the long-chain dialkyldimethylammonium salts used in the commercial production of organophilic montmorillonites, and which have been found to undergo slow but obvious decomposition, with formation of volatile amines, when adsorbed by ion-exchange on Kaycee montmorillonite.

Cetyltrimethylammonium (CTA) exchanged 'blue' and 'yellow' Kaycee montmorillonites underwent spontaneous decomposition on storage at ambient temperatures in either N₂ or O₂ atmospheres. The chloroform-extractable products were identified as consisting of a mixture of three isomeric hexadecenes, hexadecanol and a small amount of dimethylhexadecylamine, plus their homologue-derived equivalents. Trimethylamine was also found in the head-space vapours, and further quantities could be released by ion-exchange treatment of the organominerals with triethylamine. The yields of decomposition products after various storage periods are listed in Table 1. In contrast, the fully-exchanged CTA-Volcays underwent no measurable decomposition, and only trace amounts of hexadecenes or hexadecanol were obtained from the partially CTA-exchanged Al-Volclay.

The decomposition products appear to be formed by several reaction pathways, which include elimination [Reaction (1)] and retroalkylation [Reaction (2)] processes:



It is interesting that the hexadecenes appear to be formed only in the early stages of storage and disappeared on prolonged storage, probably by an acid-catalysed rehydration process with formation of hexadecanol (Galway, 1970).

The surface catalytic sites in the decomposition of CTA⁺ on the Kaycee montmorillonites have not been identified. In addition, there are not obvious analytical, spectroscopic

Table 1. Decomposition products of CTA-Kaycee montmorillonites; percentage yield mol/mol adsorbed CTA⁺

Storage time (months)	Mont.	Hexadecenes	Hexadecanol	Total
2	Blue	0.7	2.5	3.2
	Yellow	0.2	1.9	2.1
3	Blue	Trace	4.0	4.0
	Yellow	0.1	2.4	2.5
5	Blue	Trace	4.1	4.1
	Yellow	Trace	4.0	4.0

or X-ray crystallographic differences between the two Kaycee montmorillonites and the catalytically-inactive Volclay. This problem is at present under further investigation.

The spontaneous decomposition of quaternary ammonium ions adsorbed on certain montmorillonites provides a further example of reactions which may occur under ambient conditions on clay minerals, and which are of commercial consequence in the utilization of montmorillonites from a particular source.

P.O. Box 4331,
Melbourne,
Victoria 3001,
Australia

M. FRENKEL
D. H. SOLOMON

REFERENCES

- Chaussidon, J. and Calvet, R. (1965) Evolution of amine cations adsorbed on montmorillonite with dehydration of the mineral: *J. Phys. Chem.* **69**, 2265.
- Chou, C. C. and McAtee, J. L. (1969) Thermal decomposition of organo-ammonium compounds exchanged onto montmorillonite and hectorite: *Clays and Clay Minerals* **17**, 339.
- Durand, B. and Pellet, R. and Fripiat, J. J. (1972) Alkylammonium decomposition on montmorillonite surfaces in an inert atmosphere: *Clays and Clay Minerals* **20**, 21.
- Galway, A. K. (1970) Reactions of alcohols and of hydrocarbons on montmorillonite surfaces: *J. Catalysis* **19**, 330.
- Jordan, J. W. (1951) Lubricants: U.S. Pat. 2,531,440.
- Miller, R. W. and Faust, S. D. (1972) Sorption from aqueous solutions by organic clays: I. 2,4-D by bentone 24: *Adv. Chem. Ser.* **111**, 121.
- Weiss, A. and Roloff, G. (1963) Die Rolle organischer Derivate von Glimmerartigen Schichtsilikaten bei der Bildung von Erdöl: *Proc. Int. Clay Conf.*, Stockholm, Vol. 2, p. 373.