REACTIONS OF CLAY VOLATILES WITH n-ALKANES

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Abstract—Volatiles formed on heating clay minerals contain a variety of cations and anions and are highly reactive. Gas chromatograph-mass spectrometer analysis of long-chain n-alkanes exposed to such volatiles showed that some decomposition occurred even <250°C. Reactions with anions donated by the volatiles led to compounds containing atoms other than C and H, e.g., Cl. The products obtained from n-alkanes heated in a stream of clay volatiles to 500°C resembled those produced by corresponding alkane-clay mixtures heated to 250°C. At higher temperatures contact between the alkanes and montmorillonite or halloysite led to changes in the assemblages formed, whereas kaolinite or sepiolite had no effect. Thus, the first reactions that occurred when clays were heated with n-alkanes were apparently induced by the volatiles; at higher temperatures catalysis due to direct contact came into play with some of the clay minerals.

Key Words—Alkane, Catalysis, Clay volatiles, Gas chromatography, Halloysite, Kaolinite, Mass spectrometry, Montmorillonite, Sepiolite.

INTRODUCTION

Clay volatiles—the gases evolved on heating clays—have generally been implicitly or explicitly regarded as pure water. Recent investigations by Keller (1986) and Heller-Kallai *et al.* (1988) showed that this is far from the truth. In fact, clay volatiles contain a variety of chemical species, which are specific for any particular mineral and which may differ widely from one sample to another within the same mineral group. The temperature and the rate at which the various species are released from any individual mineral differ; accordingly, various assemblages of these species may be obtained from a mineral at different temperatures and under diverse environmental conditions. On condensation, liquids are obtained, which range in pH from 1 to 10. Volatiles of this kind might be expected to be highly reactive and, indeed, they have been found to attack calcite in a manner that depended on the particular clay and the specific experimental conditions (Heller-Kallai *et al.,* 1987; Heller-Kallai and Mackenzie, 1987).

The catalytic effect of clays on the thermal decomposition of organic compounds has been extensively investigated. The effect has been attributed to surface activity of the clays and to reactions in the clay interlayers. The present study addresses the question whether clay volatiles may participate in the thermal decomposition of organic matter either as catalysts or as reagents forming new compounds, which may, perhaps, trigger other reactions. Long-chain saturated hydrocarbons were chosen, because they contain only few

C–C and C–H bonds of different types and, having no functional groups, are chemically inert. Moreover, their boiling points are sufficiently high to ensure that the reagents are not vaporized before any reactions can occur.

EXPERIMENTAL

Materials

The clay samples employed are listed in Table 1. They were used as supplied, unless otherwise stated. High-purity sand was supplied by BDH Chemicals Ltd. The organic material used was of >99% purity; C24 = tetracosane ($C_{24}H_{50}$) was supplied by Aldrich, and C19 = nonodecane ($C_{19}H_{40}$) was supplied by Fluka.

Methods

The samples were inserted into a quartz reactor, 1.2 cm in diameter, which was heated in an electric fur-

Table 1. Clay samples used.

Montmorillonite, Upton, Wyoming (CMS)[1], <2-μm fraction[2]
Montmorillonite, Camp Berteau, Morocco[2]
Kaolinite, Georgia, well-crystallized (CMS)[1,2]
Halloysite, Dragon Mine, Utah[3]
Sepiolite, "Sepiolita", Tulsa, Spain[2]

[1] CMS = Source Clay Repository of The Clay Minerals Society.
[2] Analysis of the volatiles and condensates is given in Heller-Kallai *et al.* (1988).
[3] Analysis of the condensate is given in Keller (1986).

nace. Two sets of experiments were carried out: in one the organic material was physically separated from the clay, in the other the two were mixed. The organic matter was separated from the clay by plugs of quartz wool (QW) and sand. The sequence in the reactor was QW, clay, QW, sand, QW, organic matter, QW. A stream of helium (50 cm³/min) transported the clay volatiles through the organic matter and, together with the reaction products, into a trap containing glass beads and hexane and was cooled with liquid nitrogen. Externally applied hot air carried the products into the trap. To reduce premature loss of the organic matter on heating, it was placed close to the exit of the furnace to give a temperature gradient of about 150°C between the clay and the organic matter. Both temperatures were monitored by thermocouples. The temperatures given in the text, ranging from room temperature to 500°C, are those of the clay. The hexane solution was dried with $MgSO_4$, concentrated in an evaporator, and injected into a gas chromatograph-mass spectrometer (GC/MS). About 3–5 g of clay, 20 g of sand, and 30 mg organic material were used for each run. The heating rate was 10°C/min.

Two criteria were applied to ensure that no physical contact occurred between the clays and any liquid or gaseous product derived from the organic matter at any stage of the heating process. At elevated temperatures contact between the clay minerals and the organic matter caused a color change of the clay, which was easily detected. For a more sensitive test, heating was stopped at various temperatures, the clay fraction was extracted with hexane, and the concentrated solution was examined by GC. The extracts were entirely free of organic matter, confirming that the plugs were completely effective.

Instrumentation

GC/MS was carried out on a Hewlett Packard 5790A gas chromatograph directly coupled to the source of a ZAB-ZF (VG analytical) double-focusing mass spectrometer. The GC had a fused silica capillary column (length = 25 m, internal diameter = 0.3 mm) coated with Durabond-5 and used helium as the carrier gas. It was programmed at 4°C/min between 50° and 300°C, with 20 min at the maximum temperature.

The mass spectrometer operating conditions were: EI mode, electron energy = 70 eV, source temperature = 225°C, mass range = 50–500, accelerating volts = 8 kV, electrostatic sector = 800 V, computer system = digital PDP 11/24 with 96 megabytes, instrument resolution = 1000 for total ion chromatograms (TIC) (scan time 1.05 s) and 4000 for single-ion reconstruction (SIR) (scan time 60 ms per unit mass). The TIC is the record of all ions formed in the MS filed as scan numbers (translated into time) and normalized to the highest response = 100% (intensity). An SIR trace monitored the change in concentration of a selected ion with

time. In a group-type analysis (GTA), changes in the concentration of several ions were monitored simultaneously. Mass spectra, which showed the relative abundance of a single species and the associated fragments and isotopes, were derived from the TICs by computer manipulation; the relative intensities were significant provided that the signal was not oversaturated.

RESULTS AND DISCUSSION

The clay minerals used, the sand, and the quartz wool were checked for organic impurities by heating them directly in the mass spectrograph (Heller-Kallai *et al.,* 1988) and by pyrolysis in a chemical data-system (CDS) apparatus (Aizenshtat, 1982). No trace of organic matter was found.

Most of the experiments were carried out with tetracosane (C24); the results obtained with nonodecane (C19) were used for comparison only. Under the experimental conditions adopted, products of mass number less than 50 could not be detected. Moreover, in the course of trapping and concentrating the reaction products some volatile components were lost. The analyses of the product mixtures are therefore qualitative only.

If C24 or C19 were heated either alone or in the presence of sand, no decomposition occurred in the temperature range examined, i.e., <500°C, nor did dilution of the carrier gas with steam, acidified by bubbling through a concentrated HCl solution, cause any changes. In all these experiments only the original hydrocarbon was recovered.

Reactions of tetracosane with clay volatiles

Exposure of the hydrocarbons to volatiles from any of the clays studied caused some decomposition of the alkanes, even at <250°C. The distributions obtained were complex and will here be largely treated as fingerprints. A more detailed analysis will be given elsewhere.

Hydrocarbons. Figures 1a and 1c show the TICs (total ion chromatograms) obtained when C24 was exposed to volatiles derived from the Wyoming montmorillonite, heated to 250°C and between 250° and 500°C, respectively. They are similar to one another and resemble corresponding traces of saturated hydrocarbons. GTAs of hydrocarbons were computer derived from the TICs, by monitoring the expected strong molecular ions m/z = +57, +71, and +85. The similarity between the TICs and the traces of saturated hydrocarbons demonstrates that saturated hydrocarbons were the prevalent species formed. Some of the n-alkanes are marked in Figures 1a and 2a by their carbon numbers. Less intense peaks correspond to other alkanes, to branched hydrocarbons, including isoprenoids, and to cyclic compounds. Some products had carbon num-
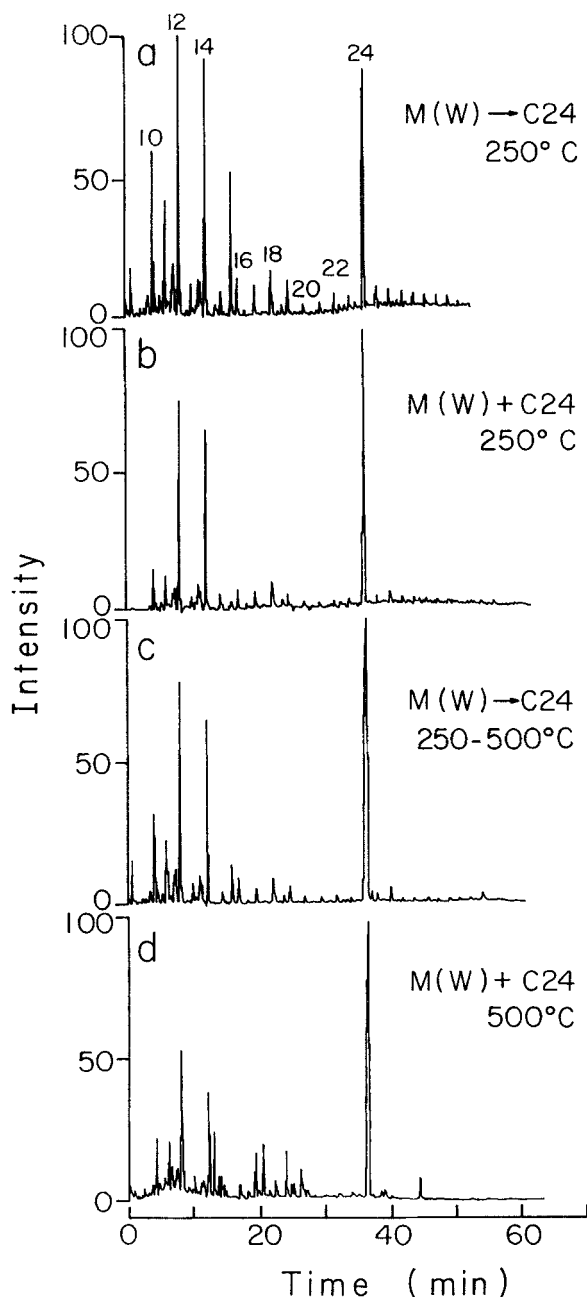
Figure 1. Total-ion chromatogram of products obtained from tetracosane with Wyoming montmorillonite: (a) volatiles, 250°C; (b) mixture, 250°C; (c) volatiles, 500°C; (d) mixture, 500°C. The carbon numbers of the dominant n-alkanes are marked in Figure 1a.

Figure 2. Total-ion chromatogram of tetracosane exposed to volatiles: (a) montmorillonite, Camp Berteau, 250°C; (b) kaolinite 250°C; (c) halloysite 250°C; (d) sepiolite 500°C. The carbon numbers of the dominant n-alkanes are marked in Figure 2a.

bers greater than that of the starting material and are of particular interest because their presence indicates that free radicals participated in the reactions. If the montmorillonite was dried at 110°C before the experiments, the reactions were enhanced.

Figure 2 shows TICs obtained from C24 heated in the presence of volatiles derived from various clays.
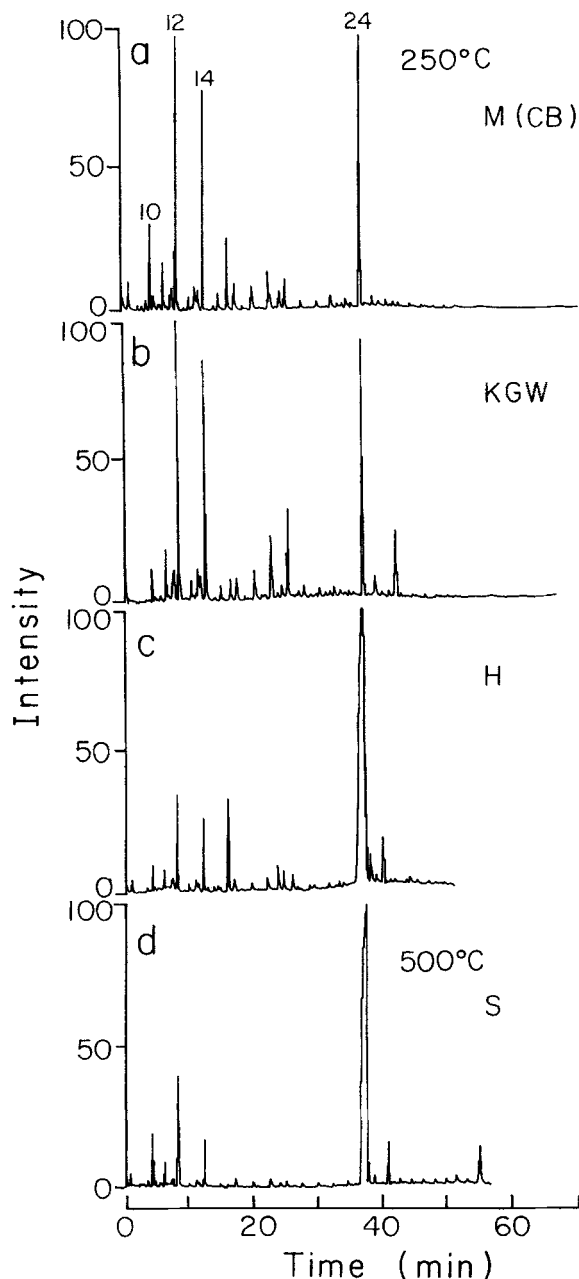
The TICs obtained on heating to 250°C are qualitatively indistinguishable from those produced on heating to 500°C. TICs produced by volatiles from different clays varied in detail, but had several features in common: (1) they all showed that decomposition of the starting organic material occurred; (2) they were dominated by straight chain alkanes; (3) some peaks due to hydrocarbons having carbon number >24 were
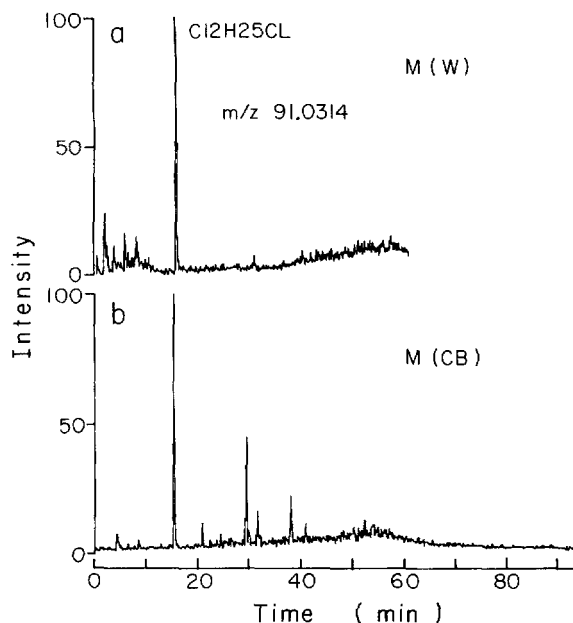
Figure 3. Single-ion reconstruction traces of $(C_4H_8Cl)^+$ in products obtained from tetracosane exposed to volatiles: (a) montmorillonite, Wyoming, 250°C; (b) montmorillonite, Camp Berteau, 250°C.

Figure 4. Single-ion reconstruction trace of $(C_8H_9)^+$ in products from mixture of tetracosane with Wyoming montmorillonite, 500°C.

present; (4) no peaks due to unsaturated hydrocarbons, including aromatics, with carbon number <24 were detected.

Alkyl chlorides. The species discussed above were composed of only carbon and hydrogen and were thus derived entirely from the organic material. Detailed analysis of the spectra showed that, in addition, some products contained heteroatoms, i.e., atoms other than C or H, such as Cl, which must have been contributed by the clay volatiles. Figures 3a and 3b are SIR traces of the chlorinium ion $(C_4H_8{}^{35}Cl)^+$, of mass number 91.0314, which is a fragment derived from alkyl chlorides. They were obtained with volatiles from the Wyoming and Camp Berteau montmorillonite samples, respectively. Both volatiles were previously shown to contain Cl (Heller-Kallai *et al.,* 1988). The parent alkyl halides were identified by their mass spectra. The natural isotope abundance ratio of ^{35}Cl and ^{37}Cl is approximately 3:1. In the mass spectra of the alkyl halides these isotopes were present in the correct intensity ratios, which confirms the assignments. The chlorinium ion was also present in the products obtained with volatiles from halloysite, in which Cl is abundant (Keller, 1986), but the volatiles from kaolinite and sepiolite, which were poorer in Cl, produced no detectable alkyl halides.

Reactions of clay-C24 mixtures

Figures 1b and 1d show the TICs obtained from mixtures of Wyoming montmorillonite with C24 heated to 250° and 500°C, respectively. In these experi-
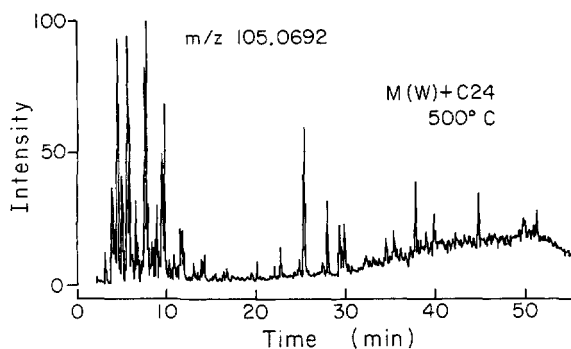
ments the temperature of the organic matter was the same as that of the clay and was therefore higher than in corresponding experiments with volatiles only. The TIC in Figure 1b is qualitatively indistinguishable from that in Figures 1a and 1c, i.e., the products obtained from the mixture on heating to 250°C were similar to those formed with volatiles only. The TIC produced by the mixture at higher temperatures (Figure 1d) differed from the other three in several respects. Figure 4 shows the SIR trace of mass number 105.0692, corresponding to $(C_8H_9)^+$, which is a characteristic fragment of aromatic hydrocarbons. In addition, different isomers of the aromatic dichloride ion $(C_6H_4ClCH_2Cl)^+$ were identified in spectra of this mixture. $(C_8H_9)^+$ was absent in products from mixtures with kaolinite, halloysite, or sepiolite, indicating that no aromatics were formed. Due to the limited amount of Camp Berteau montmorillonite available, mixtures with this clay could not be studied.

The TIC obtained from mixtures of kaolinite and sepiolite with C24 were similar to those obtained from the corresponding volatiles at all temperatures studied. With halloysite the similarity persisted only up to 250°C; at higher temperatures the mixture produced more branched and cyclic compounds. Thus, at elevated temperatures montmorillonite and halloysite surfaces exerted a specific catalytic effect on the pyrolysis of C24, whereas those of kaolinite and sepiolite did not.

Reactions with C19

Experiments with C19, both with clay volatiles and in mixtures with clays, produced assemblages that were analogous to those obtained with C24, i.e., unchanged C19 occurred together with shorter and longer chain hydrocarbons. n-alkanes were most abundant, but branched and cyclic hydrocarbons and alkyl chlorides similar to those formed with C24 were identified.

CONCLUSIONS

The most important inference from these experiments is that clay volatiles do, in fact, cause decom-

position of n-alkanes, even at temperatures as low as 250°C, whereas no decomposition occurred when the alkanes were heated alone to 500°C, either dry or in the presence of acidified steam. The mechanism of the reactions is obscure; the appearance of hydrocarbons having higher carbon numbers than the original suggests that free radicals were involved. Preliminary experiments with long-chain fatty acids and alcohols indicated that similar reactions occurred, irrespective of the functional groups present.

No differences were observed between the qualitative composition of the assemblages produced by clay volatiles alone, to temperatures of 500°C, and the corresponding clay-alkane mixtures heated to 250°C. At higher temperatures montmorillonite and halloysite exerted specific catalytic effects, whereas kaolinite and sepiolite did not.

These results have far-reaching implications for the interpretation of clay-organic reactions at elevated temperatures. The first reactions to occur between a clay and an n-alkane (and probably other organic compounds), whether in contact with the clay or not, appear to be caused by the clay volatiles. In accordance with the varying composition of the clay volatiles, their effect is specific for each mineral specimen, but some salient features are common to all the assemblages

formed. At higher temperatures physical contact with some clay minerals induced further reactions, with others it did not. Although the chemical composition of the volatiles has been determined (Heller-Kallai *et al.*, 1988), it is not known which are the reactive components.

Note that all the experiments were carried out in an open system. The same primary reactions will probably occur in a closed system, but the products formed by secondary reactions would immediately mask the initial assemblages.

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