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Reactions of Alcohols and of Hydrocarbons on Montmorillonite Surfaces

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A study has been made of the reactions of *normal* 1-alcohols (ethanol, propanol, hexanol, octanol, dodecanol and octadecanol) and of hydrocarbons (*n*-heptadecene-1 and *n*-octacosane) on a sample of natural montmorillonite, under conditions whereby the products were rapidly removed from the active surface through condensation at −196°C. These reactions yielded equilibrium mixtures of isomeric straight-chain olefins. Reactants having chain length $>C_8$ underwent significant cracking to yield products in C_4–C_8 (at least) hydrocarbon boiling range; the composition of the product mixtures were closely similar, although the absolute yields varied with the different reactants. A reaction mechanism involving initial adsorption at Lewis acid sites is proposed to account for the surface reactions, which involve double bond migration and cracking of the hydrocarbon chain. The reactions of the same alcohols, under conditions in which products and water vapour readsorption was possible, yielded mixtures consisting predominantly of branched alkanes; the production of olefins was small. There was evidence that surface reactions involved polymerization, cracking, skeletal isomerization and hydrogenation processes. All reactants gave similar product distributions and the amounts formed increased with chain length of the reactant as far as dodecanol. A reaction mechanism involving carbonium ion formation at Brönsted acid sites is proposed to account for these observations. It was concluded that the mineral enabled facile movement of hydrogen and the availability of this element was greatest where reaction conditions did not favour surface dehydration. The present results are considered to provide information concerning: (i) the properties of acid groups which occur in silica–alumina catalysts, and (ii) (not discussed in the present article) the possible participation of reactions at clay mineral surfaces in petroleum genesis.

It is well-known that the reactions of an alkene or an alkane with a silica–alumina catalyst result in the formation of complex mixtures of product hydrocarbons (*1–4*). Surface processes of some complexity are involved since the observed product distributions give evidence for the occurrence of reactions which must include cracking, isomerization, polymerization and hydrogen transfer steps. It has been concluded from mechanistic studies of such reactions that more than a single type of active site may be present on such catalyst surfaces. Pines and his collaborators (*5, 6*), working on the dehydration of alcohols on alumina, concluded that reactions may occur through a cooperative mechanism involving both acidic and basic sites. These workers also demonstrated that the activity of the catalyst, and the type of reaction which occurred, depended *inter alia* on the surface acidity, the presence of impurities (in particular, the alkali metal ions) and the methods of preparation and activation of the oxide phase. Similar patterns of behaviour may be expected of silica-alumina catalysts.

Mechanistic investigations of the reactions of organic compounds on acidic oxide surfaces have often used catalyst preparations which had previously been activated at ~500°C. Such forcing dehydration conditions may be expected to generate surface sites which may not themselves be capable of modification (in particular, hydration) during subsequent participation in surface catalytic processes. Shephard *et al.* (*3*) conclude that Lewis acid sites on their silica–alumina catalyst, previously activated at 600°C, could not readily be converted into Brönsted acid sites. Trambouze *et al.* (*7*) state the the surface acidity of silica-alumina preparations changed from protonic to Lewis-type with increase in dehydration temperature. It was therefore considered to be of interest to undertake a study of the catalytic properties of a sample of silica-alumina which had *not* been calcined and which was extensively hydrated. From such observations it was hoped to extend our knowledge of the properties of surface acid sites. Natural montmorillonite was selected as the silica-alumina phase since this hydrophilic product of a weathering process could be expected to possess fully hydrated surfaces. Furthermore, this mineral has a high surface area and is known to chemisorb organic compounds (*8*). Much of the study was concerned with the reactions of alcohols to enable comparisons with previous work on alumina catalysts (*5*, *6*).

A further reason for the present work was to investigate the possibility that the decomposition reactions of organic species chemisorbed on minerals contained in sedimentary deposits during geological periods of time provide a feasible route for petroleum genesis (*9*, *10*). A discussion of the application of the present observations to the geological environment will be given elsewhere.

EXPERIMENTAL

Reactant mixtures were prepared by adding a small quantity (~0.5 g) of the pure organic compound to (20 g) crushed montmorillonite at 20°C. Quantitative measurements of the kinetics of hydrocarbon formation from these preparations were made by an experimental technique described previously (*11*, *12*). Briefly, this method consisted of heating (after 3 hr evacuation at 10^{-5} Torr) 0.050 g of reactant at one end of a sealed tube at a constant temperature for a known time. Two sets of measurements were made in which reactions proceeded with (i) condensation of the product, and water vapour, maintained throughout the rate process by chilling the reaction tube outside the heated zone at −196°C, or (ii) the unheated end of the reaction tube at ambient temperature so that re-adsorption of initial product (and water vapour) was possible, a part of the tube being briefly chilled to −196°C during the last part of reactant heating. While chilled, the products were sealed off for subsequent analysis by gas–liquid chromatography. Qualitative product identifications were made by comparisons of retention distances with those for authentic compounds using 1 m and 3 m silicone oil and 1 m dinonylphthalate columns. Kinetic measurements were made using the 1 m silicone oil column. Sensitivity calibrations were carried out for several of the predominant products, and response characteristics of comparable hydrocarbons were assumed to be equal (*3*).

The present study was particularly directed towards the investigation of reaction products in the C_4–C_9 hydrocarbon boiling range. From examination of the yields of these compounds it was possible to estimate the relative importance of cracking, isomerization, polymerization and hydrogen transfer processes without the formation of product mixtures too complex for separation and identification. Kinetic measurements were largely concerned with the initial stages of reaction (<20%), over which obedience to the zero order kinetic equation was assumed. Some scatter of data at the highest temperatures studied is attributed to deviation from this expression with increasing extent of reaction.

Montmorillonite

A single sample of montmorillonite (No. 23 (bentonite), Chambers, Arizona; supplied by Ward's Natural Science Establishment) was used in the present work. Combustion analysis of this clay gave: H, 3.5%; C, 1.05%; and "ash," 76.9%. On heating to 200°C the mineral lost 19% of its weight by an endothermic process. The surface area of the montmorillonite, after drying at 70°C in vacuum, and measured from nitrogen adsorption at −196°C, with application of the BET equation, was 80 ± $2 m^2 g^{-1}$ (*13*). Chemical analysis of the dried clay gave: SiO_2, 64.54; Al_2O_3, 24.40%; Fe_2O_3, 1.66%; CaO, 2.35%; MgO, 5.82%; Na_2O, 0.076%; and K_2O, 0.18%.

RESULTS

Blank Experiments

Thermal desorption measurements were made for the montmorillonite as supplied, both under conditions of continuous product condensation and with product condensation only during the final stages of heating. Total product yields in the C_4–C_9 hydrocarbon boiling range were $\sim 0.02 \times 10^{16}$ and $\sim 0.1 \times 10^{16}$ mol g^{-1} from reactions at 300°C and 500°C respectively. These amounts were close to the lower limits of analytical detection and were negligible in comparison with those found when an organic reactant was present.

Reaction with product condensation at −196°C, maintained throughout. Reaction conditions ensured irreversible removal of desorbed primary products and water vapour from the active surface. Alcohols and hydrocarbons, previously adsorbed on montmorillonite at 20°C, reacted on heating to give product mixtures of straight-chain olefins. Yields of some representative alkenes, given on completion of reactions at 225 ± 25°C, are summarized in Table 1. Alkane yields were small or negligible. The chromatographic response patterns for products from the higher molecular weight reactants (that is, $>C_8$) were closely similar; comparable relative yields of the same compounds were given, although there were detectable variations between the products from the different reactants.

Ethanol and *propanol* each gave a single large response peak at low retention distance. This is attributed to ethylene and propylene, respectively. Unchanged alcohol and yields of all C_4–C_8 products were at, or below, the limits of detection ($\sim 0.01 \times 10^{16}$ mol g^{-1}).

N-hexanol gave a total yield (20 min reaction at 230°C) of 420×10^{16} mol g^{-1} of a mixture of the five *normal* hexene isomers. Complete resolution of this mixture was not achieved, but the ratio of the amount of products (*t*-hexene-2, *c*- and *t*-hexene-3) in the largest peak (1.00) to those of *c*-hexene-2 (0.456) and hexene-1 (0.068) were

TABLE 1

YIELDS OF REPRESENTATIVE ALKENE PRODUCTS FROM REACTIONS OF ALCOHOLS AND OF HYDROCARBONS ON MONTMORILLONITE UNDER CONDITIONS OF CONSTANT PRODUCT REMOVAL BY CONDENSATION AT −196°C[a]

Reactant compound	Low retention distance products[b]	*t*-Pentene-2	*t*-Hexene-2	*t*-Heptene-3	Total octenes
Ethanol	a	<0.2	<0.2	nd	nd
Propanol	a	<0.5	<0.5	nd	nd
n-Hexanol	b	~1	175	nd	nd
n-Octanol	b	2.5	2	2	200
n-Dodecanol	c	5	15	12	2
n-Octadecanol	c	8	20	17	8
n-Hexene-2	b	<0.2	~0.5	nd	nd
n-Heptene-3	b	12	15	350	nd
n-Heptadecene-1	c	2.5	12	15	12
n-Octacosane	c	10	40	70	30

[a] Yields expressed in units of 1×10^{16} mol. (g reactant)$^{-1}$; nd-below limits of detection.

[b] a, a significant yield of a single low retention distance product; b, small yields of several products; c, significant yields of several products.

close to the relative proportions of the equilibrium mixture (1.00:0.44:0.067) Furthermore, no systematic variation in the relative yields of these products was detected within the temperature range studied (90–230°C). Typical kinetic measurements for the *t*-hexene-2 formation reaction are illustrated in Fig. 1. Reactions of other organic compounds yielded the same relative proportions of isomeric *n*-hexene products, and such processes will be described below as giving an "equilibrium mixture of hexenes." The reaction of hexanol gave a further product (15×10^{16} mol g^{-1}) which remains unidentified but could have been methyl cyclopentene or a hexadiene. The extent of cracking (products $\leq C_5$) or of polymerization and cracking (products C_7–C_9) reactions were small ($< \sim 2\%$).

N-octanol gave at least five products in the octene boiling range, the total yield being $\sim 200 \times 10^{16}$ mol g^{-1}. Some cracking was also detected; this reaction gave very small yields of normal olefins including an equilibrium mixture of product hexenes.

N-dodecanol and *n-octadecanol* both underwent extensive cracking reactions to yield closely similar product distributions of *n*-C_5–C_7 olefins, including the equilibrium mixtures of hexenes. *N*-dodecanol gave the smaller relative yields of (i) octene and (ii) C_3–C_5 products.

Hexene-1 and *hexene-2* were almost completely removed during outgassing; there was some evidence of double-bond migration in the traces of olefin retained by the clay.

N-heptene-3 desorbed unchanged (350×10^{16} mol g^{-1}) and there was isomerization to *n*-heptane-2 (55×10^{16} mol g^{-1}). This reactant also underwent a very small, but just detectable, cracking reaction to give an equilibrium mixture of product hexenes.

N-heptadecene-1 and n-octacosane both yielded olefin product distributions which were closely similar to each other (larger amounts were given by octacosane) and to those obtained from the longer chain alcohols. Equilibrium mixtures of hexenes were again observed.

No systematic changes with temperatures of the relative yields of product olefins from the reactions of hexanol, dodecanol and octadecanol with montmorillonite were detected. Kinetic data for the production of *t*-hexene-2 from these reactants are summarized in Table 2.

Stearic acid gave similar alkene product distributions to those obtained from the other high molecular weight reactants. No rate process was, however, detected, though the yields increased with reaction temperature from 3×10^{16} mol g^{-1} hexene isomers given at 300°C to 30×10^{16} mol g^{-1} at 550°C.

Cyclohexanol reacted at 200°C to give 800×10^{16} mol g^{-1} cyclohexene and 200×10^{16} mol g^{-1} methyl cyclopentene as the predominant products. Trace amounts of hexenes (2×10^{16} mol g^{-1}) were also detected but the extent of cracking was small.

Reaction proceeding in the presence of gaseous products. Here primary product readsorption was possible; ~20 Torr water

TABLE 2

SUMMARY OF KINETIC DATA FOR THE FORMATION OF *t*-HEXENE-2 FROM THE REACTIONS OF ALCOHOLS ON MONTMORILLONITE UNDER CONDITIONS OF CONSTANT PRODUCT CONDENSATION AT −196°C

Organic reactant	Total yield of *t*-hexene-2 $\times 10^{16}$ mol. g^{-1}	Rate of *t*-hexene-2 production at 144°C $\times 10^{11}$ mol. g^{-1} sec^{-1}	Activation energy for *t*-hexene-2 production kJ $mole^{-1}$	Årrhenius pre-exponential factor $\times 10^{20}$ mol. m^{-2} sec^{-1}	Temperature range over which kinetic measurements were made
n-Hexanol	175	300	100.3	800	90-220°C
n-Dodecanol	15	6.1	97.4	8.1	130-240°C
n-Octadecanol	20	28	111.2	3000	120-220°C

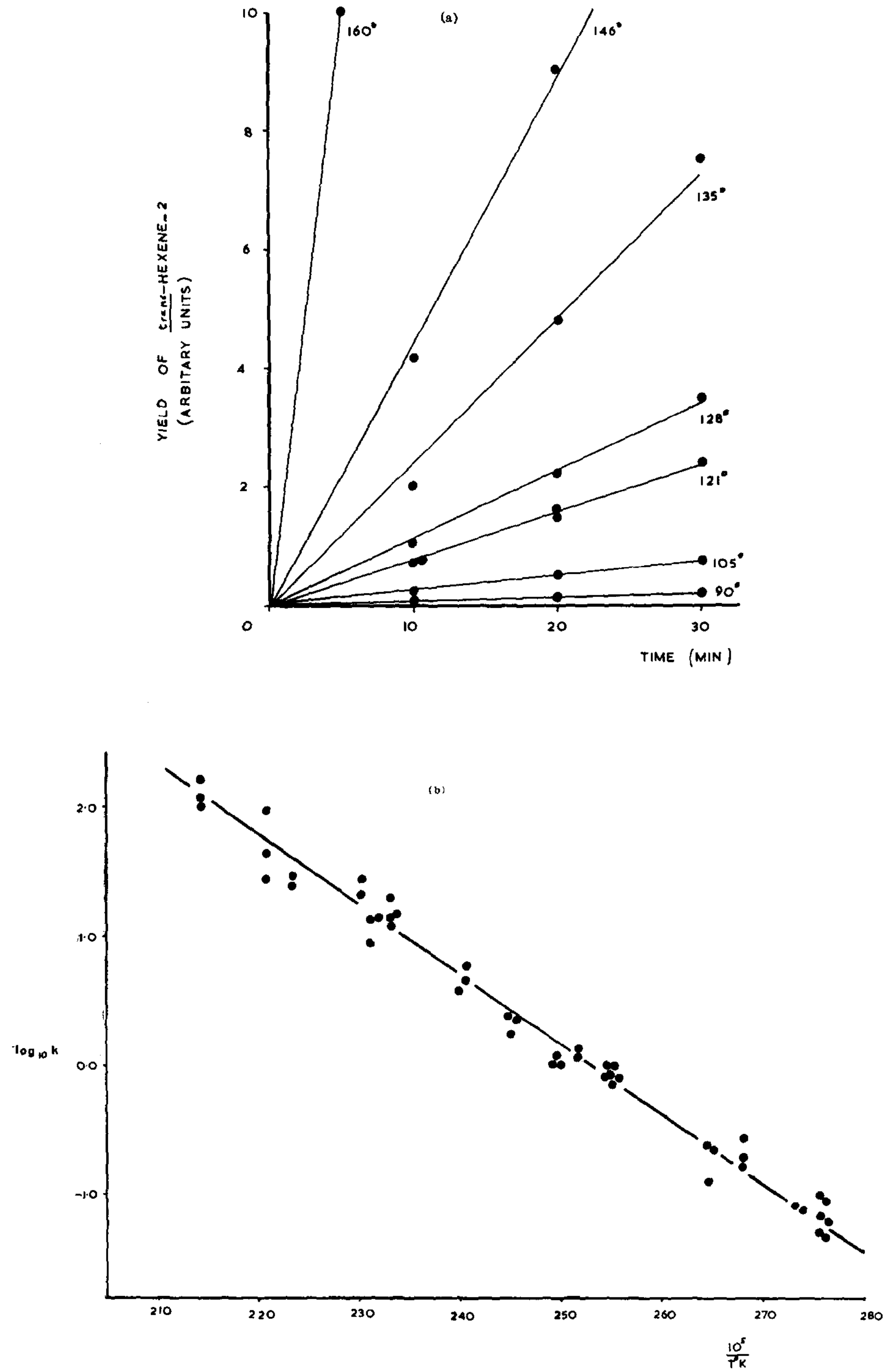


FIG. 1. Formation of *t*-hexene-2 from reaction of *n*-hexanol on montmorillonite under conditions of continual product condensation at −196°C. (a) Product yield (arbitrary units)–time plots for the early stages (<20%) of reaction at several temperatures. (b) Arrhenius plot, each point represents a single product yield–time measurement.

vapour was present over the reactant and condensation occurred in the cool part of the tube. The present work was concerned with the reactions of alcohols on montmorillonite and these yielded mixtures of alkanes in which branched chain isomers predominated. Olefin formation was small (~5%) or negligible. All the *normal* alcohol reactants studied gave closely similar product mixtures consisting of the same compounds in comparable relative yields and the absolute amounts increased with molecular weight of the reactant. Quantitative measurements of yields of representative products from reactions 225 ± 25°C are given in Table 3.

TABLE 3

Yields of Product Alkanes from Reactions of Alcohols on Montmorillonite Where Gaseous Products and Water Vapour, Remained in Contact with Active Surface[a]

	Reactants				
Products	Ethanol	Propanol	*n*-Hexanol	*n*-Dodecanol	*n*-Octadecanol
i-Pentane	<0.5	3	25	70	35
n-Pentane	<0.5	<1	3	35	20
2-Methylpentane	2.5	5	150	250	150
3-Methylpentane	1.2	2.5	50	150	70
Dimethylbutane + cyclopentane	<0.5	<1	15	30	15
n-Hexane	<0.5	<1	15	30	20
2-Methylhexane	~1	5	15	250	150
3-Methylhexane	~1	2.5	6	150	80
iso-Octanes	3	4	3	150	150

[a] Yields expressed in units of 1×10^{16} mol (g reactant)$^{-1}$.

Ethanol and propanol gave, in addition to the substances mentioned in Table 3, small amounts of the alcohol and the ether (*14*). The reactions of *n*-hexanol, *n*-dodecanol and *n*-octadecanol also yielded further products in the low ($<C_4$) and higher ($>C_8$) hydrocarbon boiling range and further minor C_4–C_8 constituents. Typical kinetic measurements for the production of 2-methylhexane from the reaction of *n*-octadecanol are shown in Fig. 2. The reaction of *n*-dodecanol on montmorillonite at 270°C gave 1500, 600, and 800×10^{16} mol g^{-1} methane, carbon monoxide, and carbon dioxide, respectively (here excess alcohol had been removed from the reactant by previous heating at 140°C in vacuum).

Zero-order rate constants for 2-methylpentane formation from the reactions of *n*-dodecanol and of *n*-octadecanol were close to a single line on the Ȧrrhenius plot. The activation energy found was 205.9 ± 5.0 kJ mole^{-1} and the frequency factor was 2×10^{34} mol m^{-2} sec^{-1} (for the desorption of this hydrocarbon only and assuming the surface area of the clay to be 80 m^{2}g^{-1}). The activation energy for 2–methylhexane production from both reactants was slightly less (195.2 ± 5.0 kJ mole^{-1}), consistent with the observed systematic change in the yield ratio (2-methylpentane/2-methylhexane) with temperature from ~0.4 at 140°C to ~0.8 at 300°C.

Cyclohexanol yielded cyclohexene, which further reacted at 200°C to give cyclohexane and methyl cyclopentane. The extent of cracking was negligible <300°C.

Discussion

Since the organic reactants studied could be distilled unchanged in vacuum, the catalytic reactions under conditions of product removal must involve material bonded to the clay surface prior to volatilization from the heated zone. It was also apparent that the products obtained were controlled by the reaction conditions and,

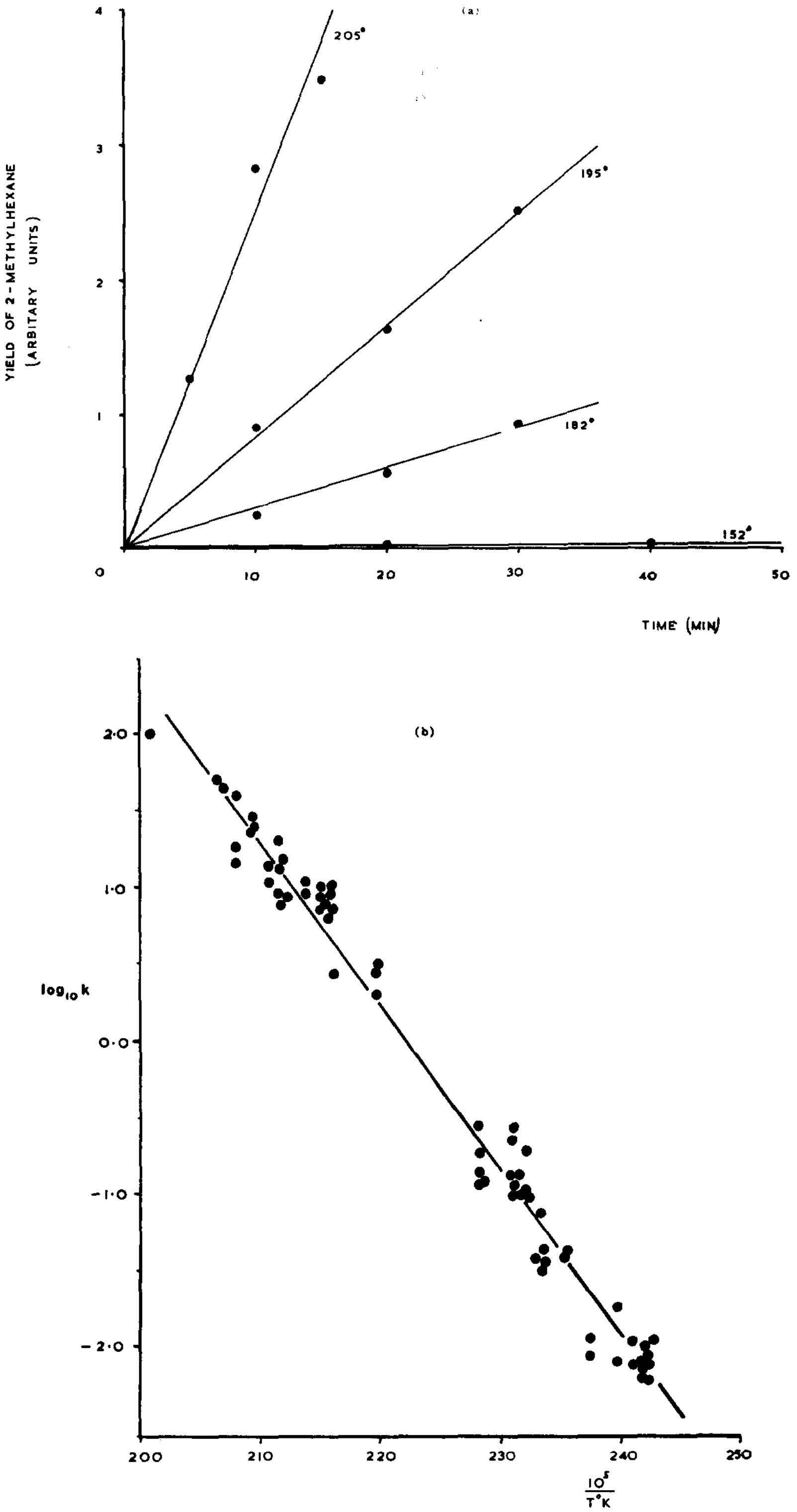


FIG. 2. Formation of 2-methylhexane from reaction of *n*-octadecanol on montmorillonite, products (and water vapour) remained in contact with reactant and were condensed immediately prior to sealing off before analysis. (a) Product yield (arbitrary units)–time plots for the early stages ($<20\%$) of reaction at several temperatures. (b) Årrhenius plot, each point represents a single product yield–time measurement.

to a less marked extent, by the organic reactant. Irreversible removal of product and water vapour yielded alkenes, whereas when readsorption was possible, alkanes were almost exclusively produced. Such formation of *either* olefins *or* paraffins contrasts with the reported behaviour of silica-alumina catalysts (*1–4*). To account for the present observations, we conclude that movements of hydrogen at the clay surface were facile. This is suggested since (i) equilibria of the surface species could be displaced to the almost exclusive production of those radicals which were the precursors to the desorption of *either* alkenes *or* alkanes, (ii) a hydrogen transfer step must precede alkane desorption, and (iii) there was "double-bond" mobility in the precursor to olefin desorption. It is appropriate, therefore, to discuss first the possible mode of movement of hydrogen at the clay surfaces, and, thereafter, the mechanisms of reactions involving adsorbed organic species.

Surface Properties of the Montmorillonite

The montmorillonite structure (*15*) may be described as two parallel planar arrays of silicon ions tetrahedrally coordinated with oxygen and, between these, an array of aluminum ions octahedrally coordinated with some oxygens of the tetrahedra and additional structural hydroxyl ions. Other cations, notably magnesium, may be present. There is invariably some replacement of silicon in tetrahedra by aluminum, together with the occurrence of a surface hydroxyl ion; these are probable sites of catalytic activity. This model, however, does not provide an adequate theoretical description for all the surface properties of the clay (*15*) and suggested alternative structures include inversion of a number of "silica" tetrahedra so that structural hydroxyl groups appear at the surfaces (*16*, *17*) and the presence of four hydroxyl groups $(\text{—OH})_4$ at silicon vacancies (*18*).

The observations mentioned in the previous section indicate facile hydrogen movements on the mineral surface at reaction temperature (>90°C). We propose, therefore, that at 90°C or above the montmorillonite phase may be represented as a resonance hybrid structure derived from several configurations in which the constituent hydroxyl groups occupy different positions. Contributory structures may include the variants mentioned above. It should be stressed that this 'band type' model is here suggested to explain the properties of a solid which may be regarded as a two-dimensional polymer; the thickness of each crystallite was of atomic dimensions, every internal atom remaining in close proximity to a "surface." On such a dynamic model, hydrogen from internal (structural) hydroxyl groups may migrate the short distance to an oxygen ion on a crystallite face; this may be accompanied by small distortions of the lattice. (This movement is formally analogous to the band theory treatment of the migration of an electron from the position of maximum stability in the vicinity of the foreign constituent in an *n*-type impurity semiconductor.) Such proton mobility in montmorillonite may be expected since (*i*) structural water loss (dehydroxylation) from the mineral at higher temperatures resulted in only small changes in the mineral lattice (a *c*-axis expansion of ~ 0.2 Å (*19*)) showing considerable structural stability and ability to tolerate some distortion, and (*ii*) superficial oxide ions are believed to attract hydrogen atoms in hydrocarbons (*20*). This resonance model may perhaps be regarded as a dynamic variant of Edelman's structures (*16*, *17*). Fripiat *et al.* (*21*, *22*) have concluded that the electrical conductivity of montmorillonite is largely determined by the migration of protons, which are present in relatively high concentration due to dissociation of water at internal surfaces. These observations are consistent with the resonance structure described above, if the interlayer water is regarded as an extension of the mineral lattice. This model may be readily modified to include bonds which are formed when organic radicals are chemisorbed.

It is difficult to define a meaningful value for the surface area of the mineral. The present measured value for partially de-hydrated (*23*) clay, 80 $m^{-2}g^{-1}$, was close to that reported by Escard (*24*) for external surfaces of montmorillonite (82 $m^{-2}g^{-1}$). Grim cites the theoretical area for clay dispersed to almost unit cell size as 800 m^2g^{-1} (*13*).

The water intercalated between adjoining montmorillonite crystallites is desorbed at ~150°C and 300°C has been (somewhat arbitarily) defined as the temperature at which loss of structural water commences (*23*). This classification does not include consideration of superficial hydroxyl groups which are, on the above model, in dynamic equilibrium with the structural water. During catalytic reactions, however, the surface dehydration processes must be further complexed by the chemisorbed organic species (*25*). The experimental observation that the products desorbed are dependent on reaction conditions strongly suggested that significant variation in surface hydrogen availability occurred at reaction temperature. Reactions were studied in the temperature range in which surface hydroxyl groups became reactive. Surface protons and dehydroxylated aluminum ions (Lewis acid sites) are sites of probable catalytic activity (*3*, *6*, *26*).

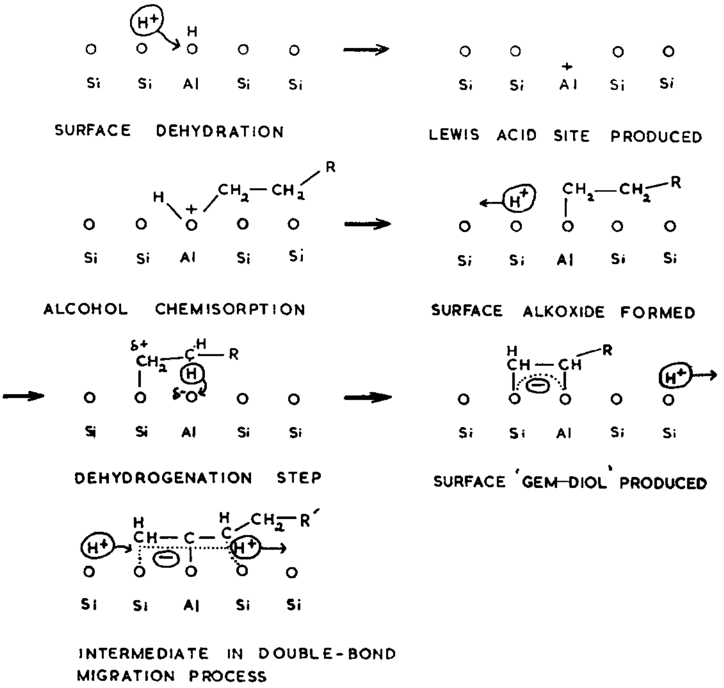
Reaction with product condensation at —196°C maintained throughout. The present experimental observations may be summarized as follows (remembering that a complete analysis of all products from all the reactions was not achieved, and specifically excluding the reaction of cyclohexanol which will be discussed separately below): (i) Reactions of alcohols and of hydrocarbons yielded mixtures of straight-chain, isomeric alkenes; there was no evidence of skeletal isomerization. (ii) Each of the longer chain ($>C_8$) reactants investigated cracked to give mixtures comprised of the same constituents in very similar relative yields. The extent of the cracking in the shorter chain reactants was less, or negligible, though these underwent facile double-bond movements. (iii) The activation energies measured for the formation of *t*-hexene-2 from all three reactants were equal (Table 2).

Taking these observations with the requirement for rapid initial reactant adsorption, we conclude that the olefin desorption step was rate-limiting. Chemisorption of the different reactants was followed by rapid changes on the clay surfaces to give comparable surface species. Consequently the energy barrier to subsequent olefin desorption was independent of the particular compound adsorbed. These reactions were observed on the mineral surface at temperatures somewhat below that (300°C) at which lattice hydroxyl group removal is observed (*23*). It may be expected that the presence of the relatively less volatile alcohol, intercalated between the laminae (*25*), together with the irreversible removal of desorbed water, would enable some surface dehydroxylation to occur, with the consequent production of catalytically active surface sites. The chemisorption of alcohol at such sites may occur rapidly after (or concurrently with) their formation. The acidic strength of such active areas enabled double-bond migration and the cracking of chemisorbed radicals to occur, but was not, however, sufficiently great to allow skeletal isomerization through carbonium ion intermediates (*6*). Furthermore, there was no significant cracking of the lower molecular weight reactants ($<C_9$). This observation is in accordance with the production of species up to at least the octenes from the cracking of higher molecular weight substances. Thus it would appear that surface cracking does not occur in radicals of chain length $< \sim C_8$. The desorption of equilibrium proportions of hexenes, and the absence of preferential alkene-1 formation, indicates facile migration of the point of surface bonding in the precursor to olefin desorption. Cracking and equilibration of double bond migrations in the chemisorbed species (adsorption probably stabilized by $C\text{–}H\cdots O\text{–}Si$ bonding (*20*)) were completed prior to desorption. The identity of the reactant molecule was, therefore, largely lost immediately after chemisorption.

No appreciable polymerization (other than ether formation (*14*)) was detected in the reactions of ethanol and propanol. It is improbable that there was significant polymerization of hexanol since this would be expected to yield the same product mixture as that resulting from the reaction of dodecanol.

The reaction of hexanol on the mineral of theoretical area 800 m^2g^{-1} (*13*) yielded 4×10^{18} mol g^{-1} of the hexene mixture. Assuming 2×10^{19} oxide ion sites m^{-2} on the clay, this corresponds to ~0.02% occupation of the surface by chemisorbed "hexenes" possibly at surface acid sites. The Ārrhenius frequency factor for hexene formation was 2×10^{23} mol m^{-2} sec^{-1}, and, taking the vibration frequency in the reaction coordinate as 10^{13} sec^{-1}, the number of sites participating in the desorption process was 2×10^{10} m^{-2} or 1 in ~2,500 of those occupied. Thus desorption was confined to a small number of sites, which may perhaps be identified with the high concentration of aluminum which occurs at crystallite edges (*27*). Similar calculations for dodecanol and octadecanol were complicated by cracking and the formation of a wider range of products.

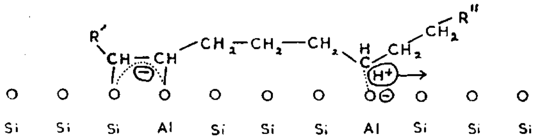
A reaction mechanism for alcohol dehydration and double-bond migration is proposed in Scheme I. Facile migration of hydrogen and location of the principal activity on superficial aluminum sites (*26*, *28*), has been assumed. The initial adsorption of alcohol at Lewis acid sites has been suggested since (i) reaction conditions favoured catalyst dehydration, (possibly accompanied by reactant chemisorption), (ii) stearic acid did not readily yield olefin products indicating that this reactant was not easily chemisorbed, (iii) the formation of olefins was inhibited by water; this is attributed to conversion of Lewis acid sites to Brönsted acid sites. It is suggested that, following adsorption, a gem-diol structure was produced which was capable of stepwise migrations across the surface and in which the position of the bond between the reactant and the surface could be changed. Movements of radical-surface bonds would be accompanied by appropriate movements of hydrogen within the crystallites. Surface radicals, at positions of intercalation, would be further stabilized through C–H···O–Si interactions (*20*).



Scheme I. Diagrammatic representation of dehydration and double-bond migration processes in reactions of alcohols under conditions of irreversible product removal.

Random migrations of such surface radicals could continue until a position of possible olefin desorption (corner, edge) was reached. This model, consisting of a succession of simple reversible steps, is proposed to account for the equilibration of surface species following adsorption and cracking steps.

The alkane octacosane bonded directly with the active mineral surface. Using this observation, Scheme I may be extended to suggest a model for the cracking process. The initial reaction occurred between a methylene group of the paraffin and a Lewis base surface site, followed (as in Scheme I) by hydrogen loss and the production of the gem-diol structure. A second occurrence of this process (Scheme II) resulted in the presence of two gem-diol groupings in the single chain. When random migrations cause their approach, this must result in considerable local strain which can be relieved through chain rupture to give two single gem-diol bonded fragments. Since bonding at a terminal carbon atom is less probable (the -1 isomer constituted ~7% of the hexene yield) and *at least* five carbon atoms must be present in the structure containing two gem-diol groups, one of which is undergoing migration, it follows that cracking may only occur in the C_7 and longer hydrocarbon radicals. This is in accordance with the experimental observations. The spacing of active groups on the surface and the availability of surface hydrogen may also influence the minimum length of chain which may be divided. These processes occur rapidly in comparison with the desorption step.



SCHEME II. Postulated step for the formation of double gem-diol intermediate suggested to occur during the cracking of chemisorbed alcohol, with subsequent olefin production, for reaction under conditions of maintained irreversible product removal. This step is closely similar to that postulated for gem-idol production in Scheme I.

This mechanism is consistent with the observations for the other hydrocarbons. *N*-Hexene is sufficiently volatile to be removed from the sample during preliminary evacuation. Some double bond mobility was possible in adsorbed heptene but the amount of cracking was very small. The longer chain reactants, both paraffins and alcohols, gave closely similar product distributions indicating that chemisorption resulted in closely comparable mixtures of surface radicals.

Cyclohexanol was the only reactant observed to undergo skeletal isomerization. Thus it was concluded that the strength of the surface acid was sufficient to allow isomerization of a ring structure but not of the unbranched chain (*6*). There was no significant opening of the ring (cracking), consistent with the view that the C_7 chain was the minimum required to form the necessary intermediate.

Reactions Proceeding in the Presence of Gaseous Products

When primary product and water vapour readsorption was possible, the reactions of alcohols included polymerization, cracking, skeletal isomerization and hydrogen transfer processes. Each of the reactants studied yielded similar relative amounts of the same products, but the absolute quantities given increased with reactant chain length up to *n*-dodecanol. The kinetic characteristics of alkane production from the reactions of *n*-dodecanol and *n*-octadecanol were identical. It is concluded, therefore, that the rate limiting step was again the desorption of product molecules from a common equilibrium assemblage of surface radicals formed after chemisorption of the alcohol. Alkenes, if desorbed, could be rapidly readsorbed and converted to the product mixture which consisted predominantly of *iso*-alkanes.

The product distribution obtained from reactions under these conditions is attributed to intermediate carbonium ion formation at Brönsted acid sites on the mineral. These reactions have been discussed previously (*1–3*, *6*). The marked variation in the product distribution with reaction conditions is attributed, therefore, to facile conversion of Lewis acid sites to Brönsted acid sites on this hydrophilic mineral.

The activation energy and frequency factor values for the formation of 2-methylpentane from reactions of *n*-dodecanol and *n*-octadecanol were both relatively high. Taking the vibration frequency factor contribution to the pre-exponential Ārrhenius term as 10^{13} sec^{-1} (as before), this corresponds to reaction at $\sim 2 \times 10^{21}$ surface sites m^{-2}, which is greater than the product yield ($\sim 2 \times 10^{15}$ mol m^{-2}), and, indeed, the 'concentration' of oxide ions at the total surface. It is concluded, therefore, that product desorption does not result from a simple desorption or decomposition process. A probable explanation is that the rate limiting step involved intermediates, the concentration of which were temperature dependent. The availability of surface hydrogen, for example, derived from water and radicals held at Lewis acid sites (*3*), may be expected to increase with temperature. This would result in a high apparent activation energy.

The yields of alkanes from reactions in the presence of ~700 Torr water vapour were small. Previous work (*29*) has shown that at low values the pressure of water vapour increased the rate of cracking reactions, but at greater concentrations the reaction rate diminished. High concentrations of water vapour may result in (i) rapid hydrolysis, with consequent desorption of the surface alcoholate, or (ii) extensive Lewis acid site hydration, with consequent inhibition of chemisorption of the hydrogen donating surface species.

The measured product yield ratio (2-methylpentane/3-methylpentane) at 220°C was 2.3 ± 0.7 (Table 3) indicating the approximate equilibration of these compounds; a similar observation, for a different system, was reported by Shephard *et al.* (*3*). The product yield ratio (2-methylpentane/2,3-dimethylbutane) was ~10, which was substantially greater than the equilibrium value (2.0–2.5) and approached the value reported by Shephard *et al.* (*3*) for a tetralin-treated catalyst. This is indicative of a high surface concentration of hydrogen and may explain the small yields of product cycloalkanes obtained from reactions on montmorillonite.

Observations for cyclohexanol showed that the acid properties of the surface were insufficient to open the alkane ring, though skeletal isomerization to methyl cyclopentane was possible.

CONCLUSIONS

The products of reactions of alcohols on montmorillonite were strongly dependent on the conditions which obtained and, in particular, whether readsorption was possible. This has been attributed to facile chemisorption of water vapour with consequent conversion of Lewis acid sites to Brönsted acid sites. Such a process contrasts with the behaviour of silica-alumina catalysts, from which mixtures containing both alkanes and alkenes are obtained (*1–4*). In making this comparison, however, several things must be pointed out.

(i) Activation of synthetic catalysts at ~500°C before reaction may cause irreversible changes in the surface active groups. In contrast, the montmorillonite was a hydrophilic product of a weathering process containing much constituent water which may be progressively desorbed by increasing the severity of the dehydration conditions.

(ii) The present low temperature reactions proceeded in the absence of a large excess of organic reactant and attention was directed to the chemical behaviour of the species which constituted the chemisorbed phase. Such processes are not necessarily truly catalytic in nature since they may be accompanied by irreversible changes which also involve the surface groups.

(iii) The large difference between the activation energy for alkene formation, where the cold trap was maintained throughout, compared with that for alkane desorption when product readsorption was possible, indicated a marked change in the catalytic processes being studied.

The band theory or molecular orbital type model proposed to account for hydrogen movements within montmorillonite may be justified since each crystallite thickness is of molecular dimensions. Each silica-alumina lamina is thus regarded as a two-dimensional polymer (or molecular crystal) across which and through which hydrogen could migrate between surface oxide ion sites and constituent hydroxyl groups. This model cannot be directly applied to synthetic silica-alumina catalysts since a lattice containing internal constituent water was not present, crystallite thicknesses were greater and the oxide had been subjected to irreversible dehydration.

It was mentioned that the present study was undertaken to investigate the possible participations of reactions at mineral surfaces during petroleum genesis. Results have shown that surface reactions yield complex mixtures of product hydrocarbons. A discussion of the application of these observations to geological systems will be published elsewhere.

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