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Selective Chemical Conversions Using Sheet Silicate Intercalates: Low-Temperature Addition of Water to 1-Alkenes

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By refluxing hex-1-ene, hept-1-ene, or oct-1-ene in hexane solution with one of a range of cation-exchanged montmorillonites, the alkenes are converted to the corresponding bis-sec-alkyl ethers. The structures of the ethers may be demonstrated by a combination of gas–liquid chromatography and spectroscopy, but they cannot practicably be prepared by any other method. A number of cations facilitate conversion, the most efficient being Cu^{2+}, Fe^{2+} and Fe^{3+}, Cr^{3+}, and Al^{3+}: Intercalation is a prerequisite for the reaction which involves transfer of oxygen from hydration shell water held in the interlamellar region to the alkene. Collapsed (strongly dehydrated) montmorillonites do not facilitate the conversion which, for the expanded silicates, is characterized by an optimal water content for a given cation. Thus for Cu^{2+}-exchanged bentonite the optimal metal–water ratio is 1:12 and under these circumstances 100% conversion of usable interlamellar water to ether is achieved. Use of other sheet structures, e.g., $Cu(UO_2)_2(PO_4)_2 \cdot 6H_2O$, failed to convert the alkenes, while with Cu^{2+}-exchanged synthetic hectorites and fluorohectorites the reaction was not clean, the ether being only one of a number of products. It has not yet proved possible to make the reaction self-sustaining by constant addition of water.

INTRODUCTION

It is well known that several members of the sheet silicate family can form interlamellar complexes (intercalates) with a wide range of organic molecules (*1, 2*). Of late, a good deal of effort has been directed toward the elucidation of the structure and properties of various stable silicate intercalates, so that much is now known about the dependence of charge density of the layered host, as well as the size and shape of the organic guest, on the degree and rate of uptake of the latter (*2, 3*). Under favorable circumstances, well-ordered stable organic intercalates are amenable to structural elucidation, usually as one-dimensional Fourier projections but occasionally in three dimensions by X-ray and neutron-beam methods (*4, 5*). However, the *dynamics* of the chemical changes that occur within the interlamellar regions remain almost completely unexplored. We are largely ignorant of the special kind of two-dimensional processes that take place between the sheets. A few spectacular examples of highly specific reactions that may be effected by heating silicate–organic intercalates have been reported (*1, 2, 6, 7*),

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but no systematic study, involving controlled variation of the reactants, has yet been carried out. In this paper we discuss, *inter alia*, the role of systematic variation of organic starting material and of exchangeable inorganic cation in the formation of secondary ethers by incorporation of water into a series of 1-alkenes, a reaction which we have discovered during the course of these studies.

Clay minerals of the type utilized by us have previously been extensively used as catalysts in a number of industrially important reactions including isomerizations, oligomerizations, polymerizations, oxidative rearrangements, and cracking of hydrocarbons (*2*, *8*, *9*). Whereas some doubt exists as to the precise location and identity of the active sites involved in these conversions, it is generally agreed that such processes are confined to the exterior surfaces, rather than the interlamellar regions, of the silicate. Frequently the function of the large area clay catalyst, especially those

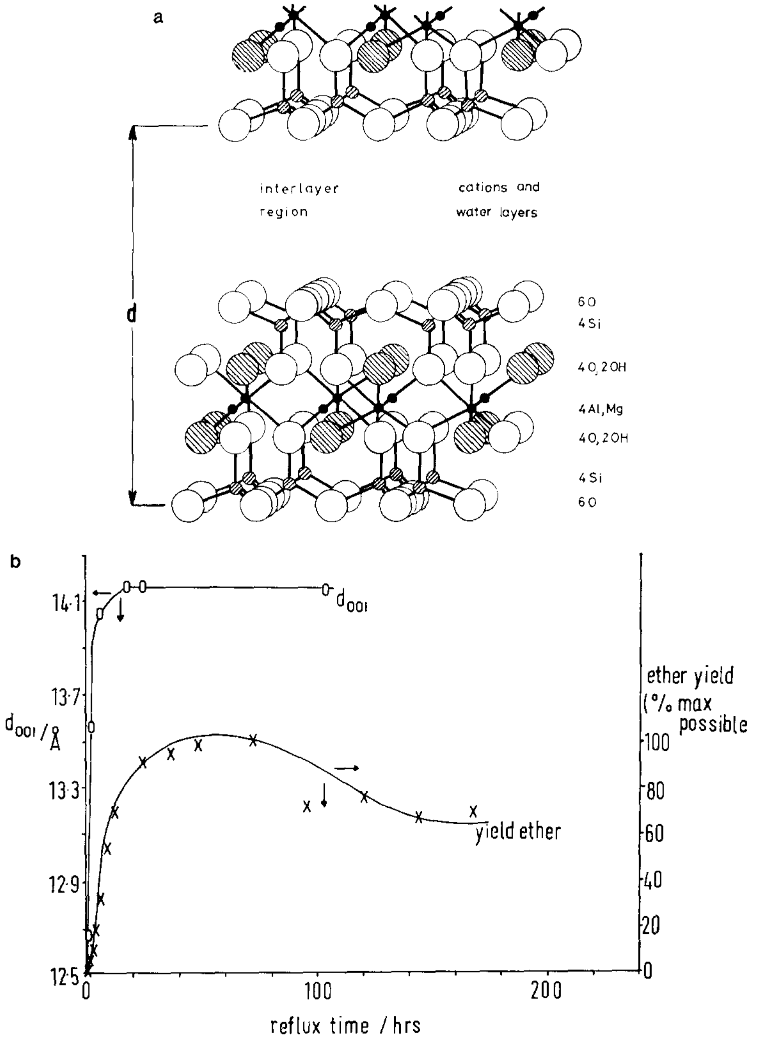

FIG. 1. (a) Schematic illustration of the structure of montmorillonite. See also Ref. (*12*). (b) Plot of the change in basal spacing of a Cu^{2+}-exchanged clay and the yield of secondary ether as a function of time.

that were acid-washed, was simply to serve as a Brønsted or Lewis acid. The type of reaction discussed here, however, is one which we believe, for reasons that are given below, takes place inside the sheet silicate host and involves a gradual depletion of reactants that are brought into appropriate juxtaposition in the intracrystallite (interlamellar) regions of the intercalate. Apart from the specificity of the reaction, the fact that it occurs at such relatively low temperatures is also particularly noteworthy. We have found that hex-1-ene is cleanly converted in the liquid phase either in solution in *n*-hexane or with self-solvent by certain metal-exchanged montmorillonites, and in the temperature range 44 to 72°C, into an oxygen-containing substance, shown to consist of both diastereoisomers of bis-2-hexyl ether. The ether is produced in quantitative yield, based on the available water initially present in the interlamellar regions (principally as bound to cations). The yield, based on alkene, is variable according to precise reaction conditions, but it was possible to account for over 65% of consumed hexene as reaction product, and in many cases, as will be seen, this consisted solely of diastereoisomeric ethers. The homologs hept-1-ene and oct-1-ene behave similarly on reflux in *n*-hexane.

METHODS

Cation exchange was affected as in our previous studies (*10*) by treating the finely divided, as received (generally Na^+-), form of the sheet silicate with aqueous solutions (generally 0.3 to 1.0 *M*) of appropriate salts for periods of ca. 48 hr. The solid was then washed repeatedly with deionized water until the excess of the cations had been removed. Surplus liquid was decanted from the solid, and the clay dried in an oven at 80°C, after which it was ground until it passed through an ASTM 150 mesh sieve.

TABLE 1

Results of GC–MS Investigation of the Pairs of "Low-Temperature" Products at 70 eV

m/e	Relative ion abundances (%)						
	Hex-1-ene		Hept-1-ene		Oct-1-ene		
	Product A	Product B	Product A	Product B	Product A	Product B	
157					14	17	$C_{10}H_{21}O$
143			17	21			$C_9H_{19}O$
129	22	25					$C_8H_{17}O^a$
113					34	32	C_8H_{17}
99			40	51	12	13	C_7H_{15}
97			12	11	10	11	
85	100	100	15	17	14	17	$C_6H_{13}{}^a$
83	4	10	21	20	17	17	
71	4	11	31	28	27	29	
69	12	19	20	23	24	20	
57	21	36	100	100	100	100	
56	8	13	21	22	19	17	
55	13	20	32	35	26	24	
45	18	13	11	11	10	11	C_2H_5O
43	76	77	60	68	64	67	
41	16	22	37	38	23	27	

[a] Determined by accurate mass measurement.

Alkenes (hex-1-ene, hept-1-ene, or oct-1-ene) were heated with the clay to reflux either neat or dissolved in alkane solvents (*n*-hexane or *n*-octane) for periods of up to 24 hr. The course of the reaction could be followed by gas–liquid chromatography. Flakes, or larger quantities, of the exchanged clay were removed periodically so as to monitor changes during reaction in such parameters as d-spacing (see Fig. 1) and infrared spectra. Once the importance of the relative humidity under which a particular cation-exchanged silicate was prepared was discovered, a series of clays was equilibrated under well-defined conditions of humidity at room temperature prior to use.

Test runs on the activity of related layered structures capable of accommodating large amounts of interlayer water were also carried out on synthetic hectorites and fluorohectorites, on beidellite, and copper uranyl phosphate.[1]

Four gas–liquid chromatographic columns were used in this study: The first, column A, a 9-ft, $\frac{1}{4}$-in.-diameter glass column packed with 3% polyethylene glycol 20 M on silanized Chromosorb G, was used for preliminary screening of reaction conditions and for measuring rate of formation of products. For the latter purpose, known quantities of nonan-5-one were added to solutions prior to analysis as a marker. The other columns were all constructed of $\frac{1}{8}$-in. external diameter stainless-steel tube: Column B of 50-ft length, contained a packing of 1.2% (w/w) hexatriacontane on silanized Chromosorb G, and the third (column C), of 6-ft length, contained 3.4% squalane on the same support. The fourth, of 50-ft length, (column D) contained 25% (w/w) Apiezon-N on silanized Chromosorb P. Column B, which was that mainly used, provided adequate resolution of higher boiling products, for initial studies of identity, when used at 125°C. Column C was used at 85°C only to separate the low and high boiling components. Column D was used only in special circumstances indicated later and was operated at 160°C.

Nitrogen carrier flow rates were optimized for maximum resolution of peaks and the sub-microliter liquid samples employed were detected on elution with a flame ionization detector.

The columns described could all readily be fitted into a gas chromatography–mass spectroscopy (GC–MS) computer system which comprised a Pye Model 104 chromatograph coupled through a silicone membrane separator to a modified AEI Model MS-9 mass spectrometer and Instem Maxi data system. Raw samples could be dealt with in this arrangement, but samples of individual products were normally trapped out in repetitive analytical GC runs with column D for ^{1}H NMR analysis on a Varian XL100 instrument and for accurate mass measurement.

RESULTS AND DISCUSSION

A. Preliminary Investigation and Identification of Products

Initial experiments showed that on self-reflux of hex-1-ene or of hept-1-ene with copper-exchanged montmorillonite, or on reflux of either of these compounds or of oct-1-ene in solution in *n*-hexane, a higher molecular weight material was produced in each case (Table 1). A sample of that formed from hex-1-ene was isolated by preparative gas–liquid chromatography, and the infrared and ^{1}H NMR spectra showed it to be an ether; olefinic features were absent.

Analysis of the reaction products on the high resolution column B showed that the

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[1] Hectorite, a trioctahedral sheet silicate, has a formula close to $(Li_{0.7}Mg_{5.3})Si_8O_{10}(OH)_4 \cdot nH_2O$. Fluorohectorites have F in place of hydroxyl groups, i.e., $(Li_{0.7}Mg_{5.3})Si_8O_{10}(OH,F)_4 \cdot nH_2O$. Beidellite is $Al_4(Si_{7.3}Al_{0.7})O_{20}(OH)_4 \cdot nH_2O$. Copper uranyl phosphate, $Cu(UO_2)_2(PO_4)_2 \cdot 6H_2O$, was kindly supplied by Dr. A. T. Howe, University of Leeds.

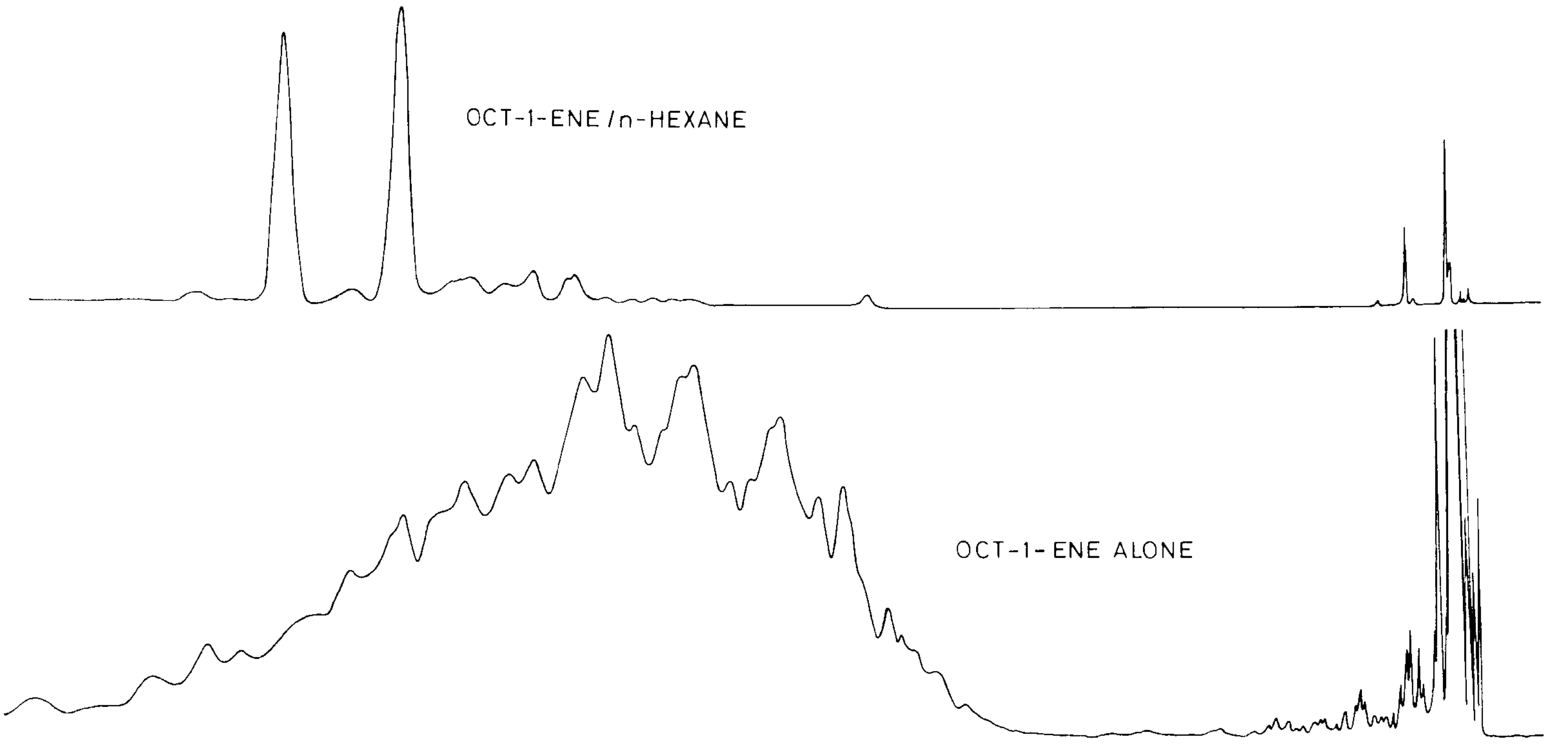


FIG. 2. Chromatograms (with column A at 125°C) of products of reaction: upper, oct-1-ene refluxed in *n*-hexane; lower, oct-1-ene self-refluxed.

products of the reaction of hex-1-ene, hept-1-ene, and oct-1-ene with metal-exchanged montmorillonite in refluxing hexane consisted in each case of a pair of compounds formed in exactly equal amounts. Similar results were obtained for the self-reflux of hex-1-ene and of hept-1-ene, but the self-reflux of oct-1-ene, i.e., at a higher temperature, gave a much more complex mixture consisting of over 40 products. Similarly complex products were formed from hex-1-ene and hept-1-ene when they were reacted in solution in *n*-octane. Figure 2 illustrates the comparative chromatograms of the oct-1-ene products: Further discussion of these products formed at the higher temperature will be deferred to a later paper, but it is clear that a major mechanistic change takes place in the temperature range 100 to 120°C.

Figure 3 shows the chromatograms of the products of the "lower" temperature reactions (*n*-hexane reflux) for all three alkenes. The products are similar pairs of peaks of retention time in the general region required for dimeric species, and when plots were drawn (Fig. 4) of the log of the retention times for each peak against carbon numbers (taken arbitrarily as C_{12}, C_{14}, and C_{16}), two good straight parallel lines were obtained. The three pairs of

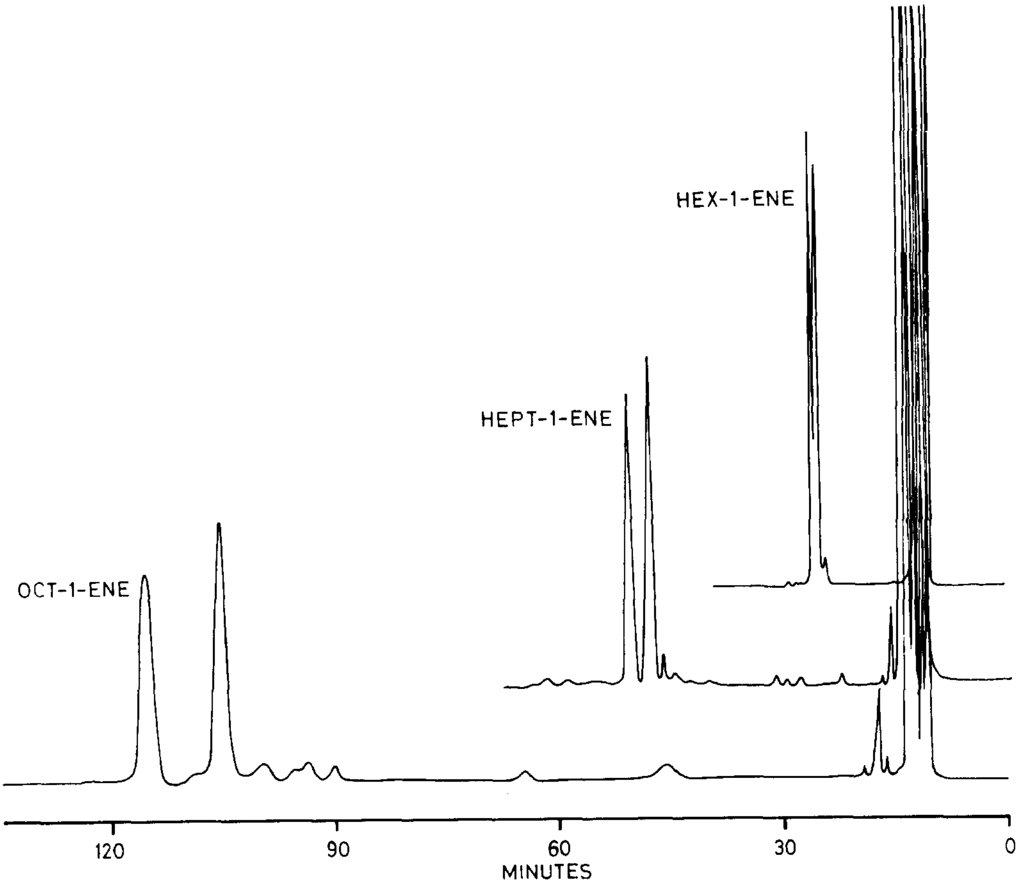


FIG. 3. Chromatograms of products of *n*-hexane reflux of hex-1-ene, hept-1-ene, and oct-1-ene with column A at 125°C. First group of peaks is solvent plus unreacted material.

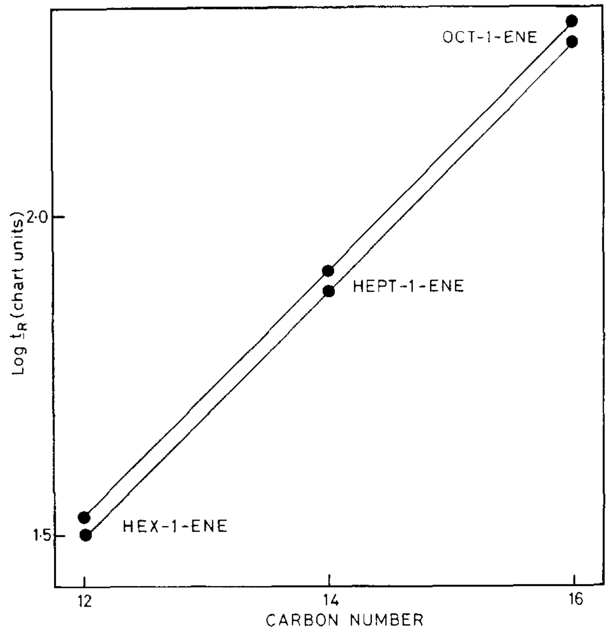
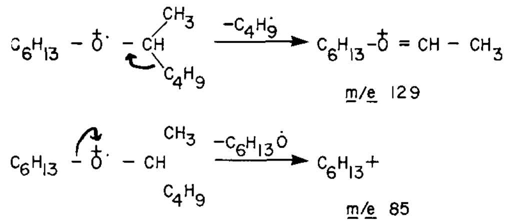


FIG. 4. Plots of log retention time (fully corrected: in arbitrary chart units) for pairs of "low-temperature" products of saturated alkene.

peaks are therefore homologs, and each is a pair of isomers with a carbon size approaching C_{12}, C_{14}, and C_{16}, respectively.

Unfortunately it was not possible to use glc retention coincidence tests to identify these products as the necessary standards were unavailable. However, a comparison with *n*-alkanes and alk-1-enes (C_6–C_{16}) showed that if they were alkenes they were branched. In view of this, and with regard to the spectroscopic evidence, we were led to consider the possibility that the three pairs were oxygenated molecules, the oxygen deriving from water in the clay.

GC–MS analysis of these "low-temperature" product pairs showed clearly that the mass spectra of each pair are very similar and that in the mass spectrometer a facile cleavage occurs. Accurate mass measurement of the significant ions yielded 129.1283 ± 0.0006 and 85.1015 ± 0.0004, which establish the ions as $C_8H_{17}O^+$(129.1279) and $C_6H_{13}^+$(85.1017). The fragmentations of these oxygenated compounds are characteristic of branched-chain hexyl ethers in which the branch is present at the C_2 position. The fragmentation would take place according to the following scheme, with the major cleavage occurring β to the oxygen atom.



Confirmation of this assignment as ethers was obtained when 1-hexyl-2-alkyl ethers were synthesized by the Williamson technique. The mass spectra of all of these compounds contained no molecular ions, but had major ions at both *m/e* 129 and 85. The 1-hexyl-1-hexyl ether, synthesized by a similar procedure, although giving a prominent ion at *m/e* 85 in its mass spectrum, gave no peak at *m/e* 129, this being replaced by a very small β-cleavage ion at *m/e* 111. Thus, we establish the presence

TABLE 2

^1H NMR Data for the "Low-Temperature" Products (τ) $CDCl_3$[a]

Hex-1-ene				
Product A	6.57 (2H sextet)	8.64 (12H, bm)	8.90 (6H, d)	9.10 (6H, bt)
B	6.56 (2H sextet)	8.65 (12H, bm)	8.89 (6H, d)	9.10 (6H, bt)
Hept-1-ene				
Product A	6.56 (2H sextet)	8.67 (16H, bm)	8.89 (6H, d)	9.1 (6H, bt)
B	6.58 (2H sextet)	8.67 (16H, bm)	8.90 (6H, d)	9.1 (6H, bt)
Oct-1-ene				
Product A	6.60 (2H sextet)	8.72 (20H, bm)	8.91 (6H, d)	9.1 (6H, bt)
B	6.58 (2H sextet)	8.70 (20H, bm)	8.90 (6H, d)	9.1 (6H, bt)
Assignment	$-CH_2-\underset{\underset{O}{\mid}}{CH}-CH_3$	$-CH_2-$	$-\underset{\underset{\underset{\mid}{O}}{\mid}}{CH}-CH_3$	CH_3-CH_2-

[a] d, doublet; b, broad; m, multiplet; t, triplet.

of a hexyl group and of a 2-alkyl group. Further, they cannot correspond to 1-hexyl-2-hexyl ether because this conclusion would not be in accord with retention times. Similarly, the GC–MS data from the pair of products from the hept-1-ene and oct-1-ene reactions are in accord with pairs of ethers in which at least one chain is branched at C_2.

F.T. ^1H NMR has established clearly (Table 2) that the two individuals of each pair are identical and that the branching in each of the two alkyl chains is at the 2-position. This would identify the hex-1-ene products as the two possible diastereoisomers (Fig. 5) of 2-hexyl-2-hexyl ether. The hept-1-ene products are the 2-heptyl-2-heptyl ethers, and the two oct-1-ene products are the 2-octyl-2-octyl ether diastereoisomers. Attempts at the synthesis of the di(2-hexyl) ethers by more usual routes gave the products of the competitive elimination processes.

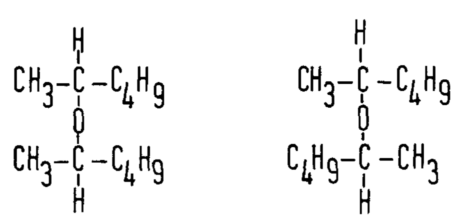


FIG. 5. The two possible diastereoisomers of 2-hexyl-2-hexyl ether.

In contrast, it proved possible to obtain good yields of 1-hexyl-2-propyl, 1-hexyl-2-butyl, di(1-hexyl), and 1-hexyl-2-hexyl ethers. Figure 6 illustrates a chromatogram (column C) in which the ethers which were synthesized were mixed with a Cu^{2+} clay/*n*-hexane-reacted sample of hex-1-ene.[2] The peaks in order of emergence are [1] 1-hexyl-2-propyl and [2] 1-hexyl-2-butyl ethers, [3] reaction products, and [4] 1-hexyl-2-hexyl and [5] di(1-hexyl) ethers. A plot of log (retention) against carbon number for peaks 1, 2, and 4 gives an excellent straight line, while the difference in log (retention) for di(1-hexyl) and 1-hexyl-2-hexyl ethers subtracted from that for the latter provides a value of log (retention) midway between the values for the two product peaks. This offers a high degree of confirmation of identity. It is an interesting fact that the small peak between peaks 2 and 3 is in exactly the right position to be the 1-hexyl-2-pentyl ether which could arise from

[2] Almost invariably the clay minerals we have investigated belong to the so-called smectite family consisting of tetrahedral (T)–octahedral (O)–tetrahedral (T) sheets bearing a negative charge. Montmorillonite typifies this family, and bentonite, a naturally occurring assemblage of clay minerals, is usually rich in montmorillonites.

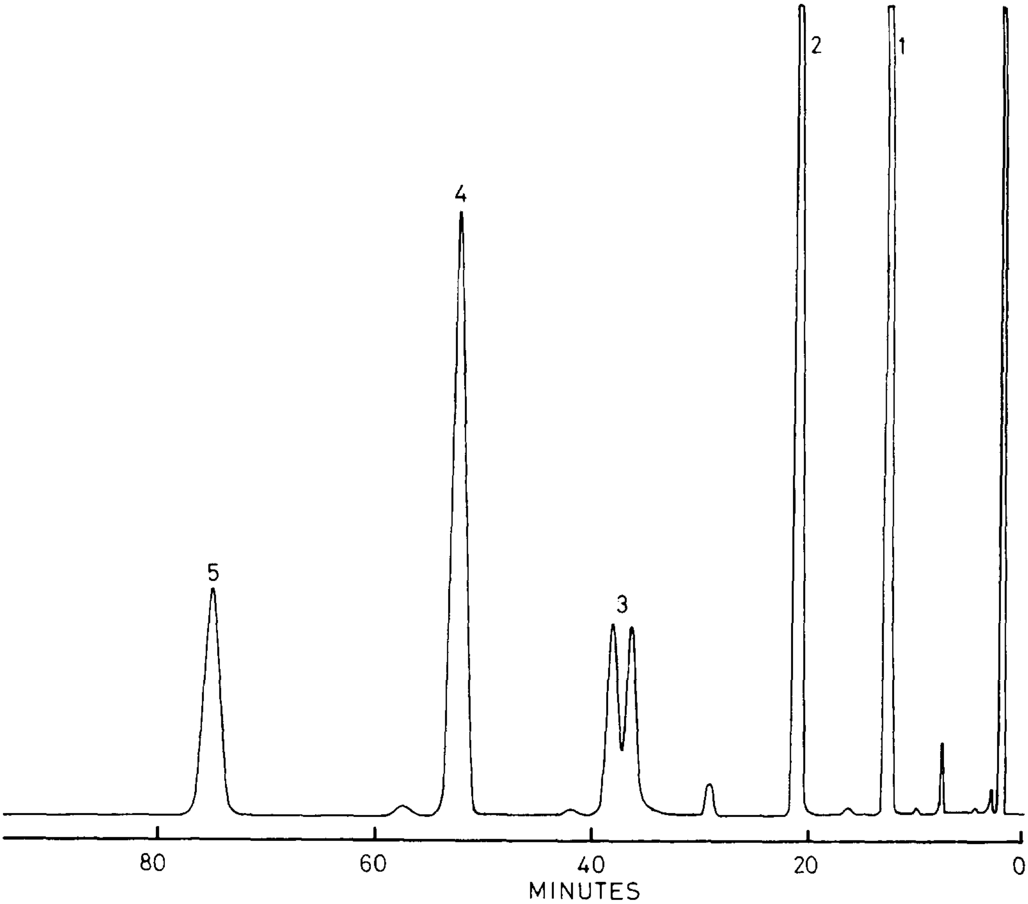


FIG. 6. Chromatograms with column C at 160°C of synthesized ethers: (1) 1-hexyl-2-propyl, (2) 1-hexyl-2-butyl, (4) 1-hexyl-2-hexyl, and (5) 1-hexyl-1-hexyl. (3) "Low-temperature" reaction product of hex-1-ene in *n*-hexane.

pentanol impurity in the butanol used for synthesis of the 1-hexyl-2-butyl ether.

Figure 7 finally shows a chromatogram of a mixture of the synthetic ethers with the highly concentrated residue from the attempted di(1-hexyl) ether synthesis with sulfuric acid. It is clearly identical with that of Fig. 6, and so, although we have been unable to synthesize a sample unambiguously, there can remain no doubt of our identification. Indeed, it is a remarkable feature of the work that the synthesis of these difficult ethers is so facile in the clay experiments.

B. Further Investigations

The reaction conditions and the nature of the reaction products having thus been established, we set about answering a number of important mechanistic questions. Is the reaction genuinely confined to the interlamellar regions, or does it take place at the external surface of the solid? Since water is consumed in the reaction, is it extracted from the solvation shell of the interlamellar cations or from the "structural water" of the sheet silicate, which is known to contain OH linkages attached to octahedrally coordinated cations? Are there optimum degrees of hydration of the metal-exchanged sheet silicate for a given interlamellar ion, and are some cations more efficacious than others in facilitating the conversion of the alkene? Since montmorillonites vary greatly in chemical behavior, especially so far as ease of intercalation is concerned (depending upon their geological origin), it is necessary to establish whether some commercially available sheet silicates are more effective, following ion-exchange, than others. These questions have been answered, at least in part, but there remains the problem as to whether there are competing reactions which might possibly be "tuned" by judicious selection of experimental conditions, and this will be taken up in a later publication.

It transpired that almost all sources of available mortmorillonite exhibited marked activity, following ion-exchange, as agents for the reaction. Although the majority of our work entailed use of commercially available bentonite (Hopkin and Williams) —of cation exchange capacity (*11*), 66 meq/100 g air-dried alumino silicate—the following solids are also remarkably active: Volclay (American Colloid Co.), Girdler-K10 (Sud-Chemie, Munich), BDH ben-

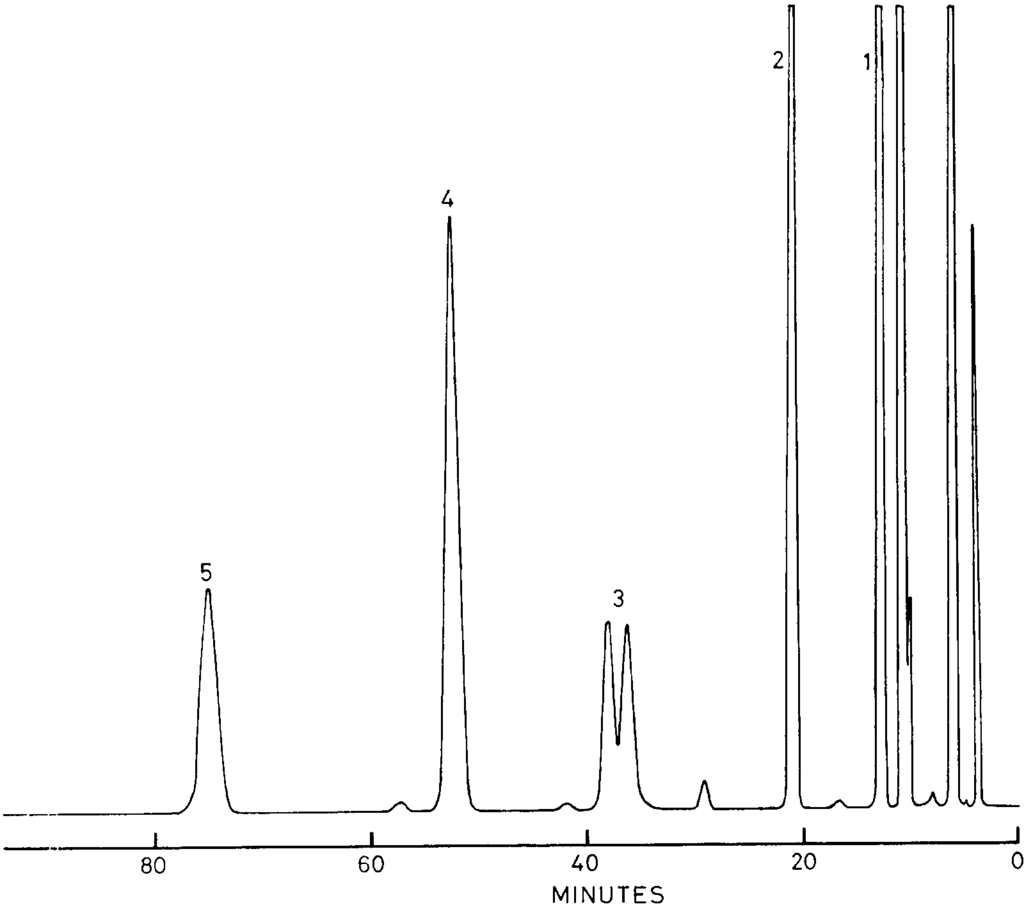


Fig. 7. Chromatograms with column C at 160°C of synthesized ethers; (1) 1-hexyl-2-propyl, (2) 1-hexyl-2-butyl, (4) 1-hexyl-2-hexyl, and (5) 1-hexyl-1-hexyl. (3) Concentrated residue from the attempted synthesis of 2-hexyl-2-hexyl ether. Extra early peaks (cf. Fig. 6 result from competitive elimination reaction).

TABLE 3

Characterization of the Clay (and Other) Species

Clay	d 001 (Å)	H_2O (%)	Number of H_2O's/cation[a]	Ether[b] (mol%)
Cu^{2+}	12.6	6–8 (one-layer)	10	3.7
Cu^{2+}	14.7	10–12 (two-layer)	17	0.32
Cu^{2+}	16.2	14–18 (three-layer)	25	0.02
"Collapsed" Cu^{2+}	9.26	—	—	Negligible
Cu^{2+}-Laponite B	12.0	10.2	13	0.25
Cu^{2+}-Laponite XLG	12.0	10.5	14	0.28
Cu^{2+}-kaolinite	7.2	—	—	—
$Cu(NH_3)_4^{2+}$	12.5	—	—	—
$Cu(NH_3)_4^{2+}$ after hexene reflux	12.3	—	—	—
Co^{2+}	15.0	9.2	15	0.55
Co^{2+} after 24-hr hexene reflux	13.5	—	—	—
Fe^{2+}	11.2	7.2	11.5	2.4
Fe^{2+} after 24-hr hexene reflux	13.8	—	—	—
Fe^{3+}	12.9	7.9	19	3.2
Fe^{3+} after 24-hr hexene reflux	13.8	—	—	—
Na^+	12.3	2.2	1.8	0.2
Na^+ after 24-hr hexene reflux	11.5	—	—	—
Cu^{2+} after 100-hr hexene reflux	14.2	—	—	—
$Cu(UO_2)PO_46H_2O$	8.9	10.9	6	Negligible

[a] Number of H_2O's/Cu based on clay cation exchange capacity of 70 meq/100 g clay.

[b] Based on 0.5 g clay/5 ml hexene reflux.

tonite, montmorillonite provided by the Steetley Co. Ltd., and Fuller's earth (iron-rich montmorillonite) from Woburn.[3] X-ray diffraction traces of all these ion-exchanged clays were qualitatively similar.

C. Product Yield as a Function of Time and Water Content of Exchanged Silicate

Experiments carried out on all three different hydrated forms [the so-called one (water)-layer, two (water)-layer, and three (water)-layer variants, see Table 3] of the Cu^{2+}-exchanged clay showed that the yield of ether first gradually increased, reached a maximum and then fell away (Fig. 8), this fall off deriving from the efficiency of the dehydrated clay as a cracking catalyst. The time scales of such changes were, however, very different, the more rapid production and subsequent fall-off of ether yield being greatest for the one-layer silicate. It is to be noted that whereas quantitative use, for ether production, is made of all the interlamellar water in both the one-layer and the two-layer silicates, only about a fifth of the water is utilized in the three-layer form. With other, structurally distinct layered solids containing interlamellar Cu^{2+} in a water-rich environment [e.g., Cu $(UO)_2(PO_4)_2\cdot 6H_2O$], there was no detectable production of the hexyl ether. Clearly the ease of utilization of the water is a function of both the water content and exchangeable cation in the interlamellar region, as well as of the host solid. Indeed it is noteworthy that the effect of the lattice is more subtle than just allowing the reaction to proceed or otherwise. With some of the exchanged silicates (e.g., Cu^{2+}-exchanged synthetic hectorite) a wide range of products is obtained including the ether, whereas with the Cu^{2+}-bentonite the reaction proceeds much more cleanly.

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[3] It has long been known that Fuller's earth is an effective catalyst for a variety of reactions; see, e.g., Thomas and Rideal (*12*).

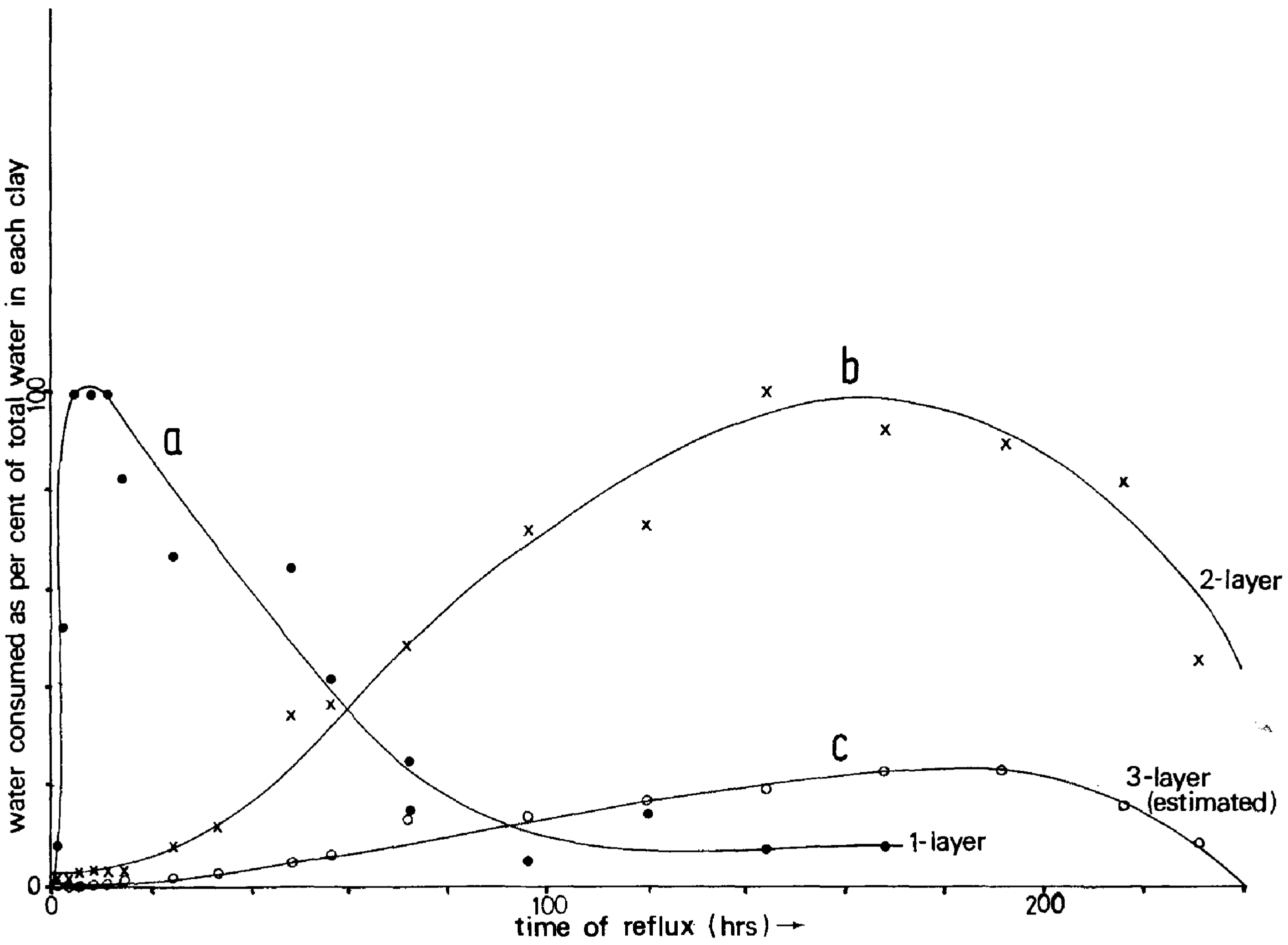

FIG. 8. Yield of ether vs time for (a) one-water-layer, (b) two-water-layer, (c) three-water-layer Cu^{2+}-exchanged clay. In each case 5 g clay (when air dry) was equilibrated at an appropriate relative humidity and then refluxed in a solution of 34.2 g hexene.

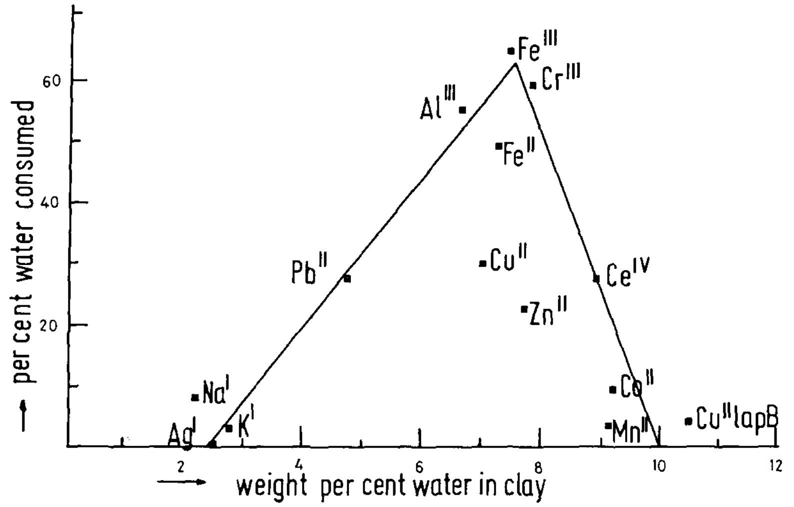

FIG. 9. Plot of percentage of water consumed as percentage of water in clay after a 5-hr reflux (0.5 g clay equilibrated at 22% RH at 21 °C in 3.42 g hexene). Note that the Fe^{2+} clay has probably oxidized to Fe^{3+}.

D. Product Yield and the Nature of the Exchanged Cation

A systematic study of the combined role of interlamellar water and cation was carried out by using specific cation-exchanged clays that had been prepared under conditions of humidity which controlled the degree of hydration of the interlamellar space (and, therefore, the degree of hydration of the exchangeable cation). The results are summarized in Figs. 9 and 10 which are reminiscent of the "volcano" plots obtained in other, not unrelated heterogeneous reactions.[4]

The most noteworthy feature of Fig. 9 is that an optimum amount of interlamellar water is required for efficient conversion of the alkene to the ether. The fact that the peak position shifts to lower water contents (compare Fig. 10 with Fig. 9) when there is a systematic drop in water content associated with each interlammelar cation serves to underline the importance of the joint role of cation and its associated water. It implies also that for a given so-called "one-layer" Cu^{2+}-exchanged clay a range of water contents may exist and that there is an optimal value for the Cu/H_2O ratio, within that "one-layer" phase, at which conversion rates are at their most efficient. It turns out, from separate experiments which also yield a volcano plot for the Cu^{2+}-exchanged clay itself, that this optimum ratio is $Cu:H_2O = 1:12$.

E. Is the Reaction Genuinely Interlamellar?

Figure 1b offers strong evidence for the view that intercalation is a necessary precondition for the reaction leading to ether formation. This fact, taken together with the following, makes it likely that conversion occurs only in the interlamellar regions:

(a) No ether is produced on collapsed clays or on any cation-exchanged varieties which, for other reasons, are incapable of intercalating the various alkenes used in this study;

(b) When $Cu(NH_3)_4^{2+}$ ions were exchanged, from aqueous solution, with a parent bentonite the resulting sheet silicate showed no activity for ether production or

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[4] "Volcano" plots have been obtained in the heterogeneously catalyzed decomposition of formic acid, ethylene hydrogenation, and deuterium exchange with ammonia (*13–15*).

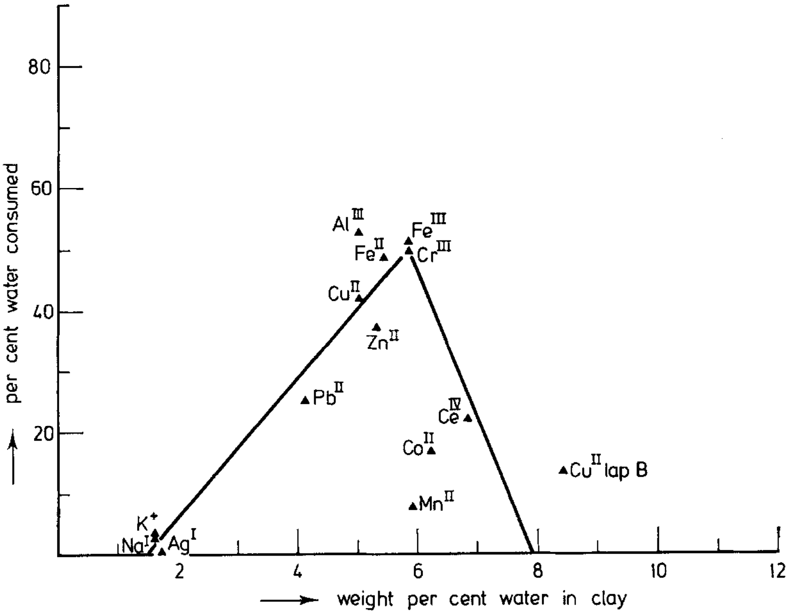

FIG. 10. Plot of percentage of water consumed vs percentage of water in clay after a 5-hr reflux (0.5 g clay equilibrated over anhydrous $CaCl_2$ at 21°C in 3.42 g hexene).

any aptitude (as deduced from d-spacings) for intercalation itself;

(c) When pyridine is taken up in the interlamellar spaces of the Cu^{2+}-exchanged clay, no ether is subsequently produced.

A few other relevant facts merit comment. Synthetic clays Laponite XLG and Laponite B differ from one another only in respect to the fact that the octahedral Mg^{2+} ions of the first sheet silicate—they are both hectorites—coordinate to OH^- rather than F^- ions as in the latter. That there was no difference in behavior between these two clays substantiates the view, which has been established in sections B and C above, that structural water (often designated as lattice water, i.e., the OH^- groups in this instance) is unimportant in the ether production.

Thus it would seem that the rather unusual properties of the water molecules belonging to the hydration shell of the interlamellar cations are of vital importance in this reaction. Much previous work by pulsed nuclear magnetic resonance and other techniques (*16–20*) has shown that this water is of extremely high acidity with reported dissociation constants of the order of 1 liter mol^{-1} at room temperature. In other interlamellar processes, such as the transalkylation reaction $2RNH_3^+ \rightarrow R_2NH_2^+ + NH_4^+$, it has been shown (*20*) that this highly dissociated water has a dominant influence, and indeed the suggestion that this acidic water could be of fundamental importance in clay catalysis was made some time ago (*17*), while in the liquid phase acid-catalyzed addition of the elements of water to olefins is a well-known process.

F. Conclusions

We have shown that:

(a) Intercalation is a precondition for a novel reaction which entails the incorporation of oxygens present initially in interlamellar water into 1-alkenes with formation of a secondary ether when a metal-exchanged hydrated clay is brought into contact with the liquid hydrocarbon in the range 44 to 100°C (cleanest product obtained below 72°C).

(b) The reaction efficiency is, *inter alia*, governed by the nature of the interlamellar cation and its degree of hydration.

(c) One-hundred percent efficiency, computed on the basis of the usable interlamellar water, may be achieved under certain conditions. The total yield of secondary ether is greatest when a "two-layer" clay, with an optimum H_2O:cation ratio (i.e., 12:1 for $H_2O:Cu^{2+}$), is used, 1.5 g of ether being obtained from 1 g of clay.

(d) It has not yet proved possible to make the reaction self-sustaining by constant addition of water. Problems relating to miscibility arise.

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