JOURNAL OF CATALYSIS 78, 197–208 (1982)

Catalyzed Reactions of Organic Molecules at Clay Surfaces: Ester Breakdown, Dimerizations, and Lactonizations

JOHN M. ADAMS, S. ELIZABETH DAVIES, SAMUEL H. GRAHAM,[1]
AND JOHN M. THOMAS*

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, Wales, and
** Department of Physical Chemistry, Lensfield Road, Cambridge CB2 1EP, England*

Received February 25, 1982; revised June 7, 1982

The use of montmorillonites as Brønsted acid catalysts has been investigated for a range of reactions: (i) decomposition of cyclohexyl esters, (ii) dimerization of propenylbenzenes, and (iii) the lactonization of cyclooctene-5-carboxylic acid. The ester cracking can be accomplished with a wide range of ion-exchanged clays, with conversions of up to 98% after 7 hr at 140°C (Al^{3+}-montmorillonite). Although the cracking rate is dependent upon the interlayer cations in the clay, at least some of the activity is due to sites on the external surfaces of the clay particles. The dimerization of anethole (1-(4-methoxybenzene)-prop-1-ene) is efficient when using either di- or trivalent cation-exchanged montmorillonites, e.g., 44% recoverable yield of metanethole is attainable in 1 hr at 126°C compared with literature procedures giving 24% yields in 7 hr. For a second propenylbenzene, isohomogenol (1-(3,4-dimethoxybenzene)-prop-1-ene), dimerization could only be effected using the very acidic trivalent ion-exchanged montmorillonites. Yields were typically 60% after 5 hr at 69°C. It is not apparent why there are large differences in reactivity between anethole and isohomogenol, which are closely related structurally. Cation-exchanged montmorillonites can also catalyze the conversion of cyclooctene-5-carboxylic acid initially to 4-cyclooctane carbolactone and then to a variety of other lactone products. The rate of consumption of the acid is similar with a variety of ion-exchanged clays, but the subsequent rate of isomerization is cation dependent. For the lactonizations the clay acid catalysts proved no better than liquid phase catalysts in producing a high percentage of one particular lactone.

INTRODUCTION

As part of a wide-ranging program of studies of intercalation of organic molecules by a variety of naturally occurring and modified sheet silicates, we have previously reported several novel organic reactions that take place efficiently either within the interlamellar regions or at the exterior surfaces of montmorillonite clays (*1*).

The clays are first subjected to ion-exchange and it has been found that the following interlamellar cations confer significant catalytic properties upon the silicate: Al^{3+}, Fe^{3+}, Cr^{3+}, and Cu^{2+}. Brønsted acidity has been shown to be responsible for many of the processes that include amine (*2*), ether (*3, 4*), and ester formation (*5*). Here we report upon (i) the catalyzed thermal decomposition of three cyclohexyl esters to cyclohexene and the corresponding acids, (ii) the dimerization of selected propenylbenzenes, and (iii) the lactonization of cyclo-octene-5-carboxylic acid.

METHODS

A sample of bentonite (ex Hopkin and Williams) was dispersed in water and that fraction possessing a particle size less than 2 μm collected. In this process the montmorillonite component was separated from impurities. Cation exchange was effected by immersion of this fraction in 0.5–1.0 mol dm^{-3} solutions of appropriate salts. The clay was washed several times to remove excess salt, and then dried at ca. 50°C. The amount of water initially present in each of

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[1] Deceased.

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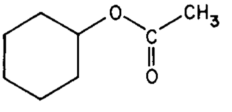
these catalysts was determined by thermogravimetric analysis. For some experiments "collapsed" clays were prepared by heating the appropriate cation-exchanged variety to 350°C for 24 hr: for such material once the interlamellar water had been removed the clay failed to reexpand on exposure to water or organic species and only the external surfaces are available for reaction with such catalysts. Reactions were carried out typically under reflux, thus the ester breakdown studies were conducted in this fashion using xylene as solvent. Product analysis was effected mainly by gas liquid chromatography (GLC) and confirmed by proton nuclear magnetic resonance (NMR).

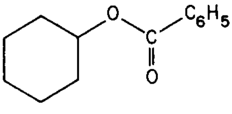
RESULTS AND DISCUSSION

1. Thermal Decomposition of Cyclohexylethanoate, Cyclohexylbenzoate, and Cyclohexyltrimethylethanoate

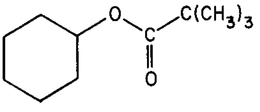
The above-named cyclohexyl esters are known to undergo decomposition into cyclohexene and the corresponding acids at temperatures above 400°C over pyrex or quartz surfaces. Since cyclohexene, unlike most other olefins, does not undergo further reaction in the presence of montmorillonite (*6*), these esters constitute a convenient family for assessment of the efficiency of the exchanged sheet silicates in catalytic breakdown.



cyclohexylethanoate



cyclohexylbenzoate



cyclohexyltrimethylethanoate

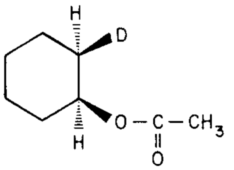
An initial study was made using cyclohexylethanoate and an Al^{3+}-exchanged montmorillonite. With xylene as solvent (bp 140°C) high conversions of the ester were accomplished in 7 hr. Different ratios of clay catalyst to ester were used to optimize reaction conditions. It was observed that increasing the catalyst concentration beyond 0.2 g in 5 cm^3 of a 10% solution of cyclohexylethanoate in xylene did not increase the rate of disappearance of the ester—probably due to mixing problems. The catalyst gave essentially identical yields in successive experiments; no other products apart from the appropriate acid and cyclohexene were detected. (An 18 ft butanediol succinate on chromosorb G column was used with nonan-5-one as marker for quantitative GLC.)

For comparison, several alternative catalysts, zeolite 4A, zeolite 13X, a commercial catalyst known as K10 derived by acid treatment of a bentonite (Sud-Chemie), and a synthetic fluorohectorite (Laponite XLG) all ion-exchanged with Cu^{2+} were also tested (Table 1). Clearly, most of the metal ion-exchanged montmorillonites are efficient catalysts for the breakdown; but the collapsed clays exhibit more varied behavior. Removal of the water from the Cu^{2+}-exchanged clay destroys the activity, whereas for the Co^{2+} and Al^{3+} analogs, activity is still maintained but at a diminished level. This means that, for these two solids at least, the external, as well as the interlamellar, surfaces are catalytically active. The results for the other Cu^{2+}-exchanged solids are broadly as expected. For the

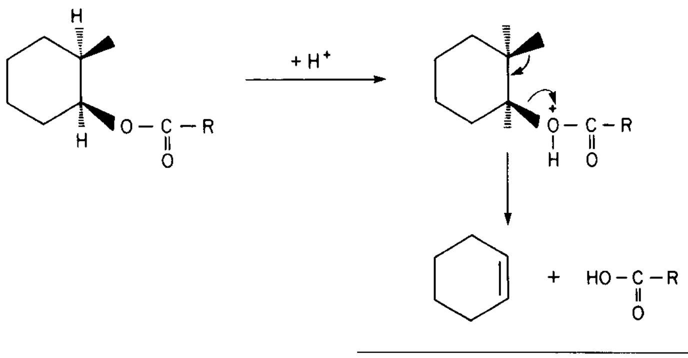
Cu^{2+}–zeolite-A the cage apertures are too small to permit access of the organic reactant to the transition metal ion in the α-cage, a situation different from that obtained in the faujasite-based X-zeolite. The latter does display some catalytic activity, though rather less than the Cu^{2+}-exchanged hectorite which, being a sheet silicate, is more comparable to the Cu^{2+}–montomorillonite catalyst and the Cu^{2+}-treated K-10.

It was established that interlamellar water is not a prerequisite for the ester breakdown. (The catalyst was prerefluxed in xylene to replace the interlamellar water with xylene: the amount of water collected in a Dean and Stark trap agreed with that initially present in the clay and thermogravometric analysis showed that the intercalated xylene now constituted 5% by weight of the montmorillonite.) The basal spacing changed from 12.5 to 12.3 Å on replacing water by xylene and the (001) X-ray reflection broadened somewhat, indicating the onset of some crystallographic disorder. The catalytic efficiency of this "xylene" intercalate was found to be essentially indistinguishable from its "water" analog.

Repeat experiments using cyclohexylbenzoate yielded essentially the same results as with the cyclohexyethanoate. Furthermore, when cyclohexyltrimethylethanoate was used (with the Al^{3+}-exchanged catalyst) the rates of thermal decomposition were closely comparable to those obtained with the cyclohexylethanoate with the same catalyst. This fact, signifying as it does the absence of any significant steric effect suggests that the breakdown proceeds via a *cis* rather than a *trans* mechanism. This, in turn, indicates that a *cis* pyrolysis, rather than a hydrolysis followed by a *trans* dehydration, constitutes the essential feature of the breakdown (Fig. 1). Further support for this view comes from experiments with the deuterated species:



If *trans* elimination takes place we would expect the deuterium to be retained within the cyclohexene. A GLC/mass spectrometric study of generated cyclohexene revealed, however, that some 17% of this was not deuterated. This is significantly less than expected on a statistical basis and is thought to be due to a primary kinetic isotope effect. A plausible mechanism, in line with the Brønsted acidity of these clays would be:



2. *Dimerization of Propenylbenzenes*

Anethole (I, 1-(4-methoxybenzene)-prop-1-ene) and isoeugenol (IV, 1-(3-methoxy-4-hydroxybenzene)-prop-1-ene) are both known to dimerize under certain circum-

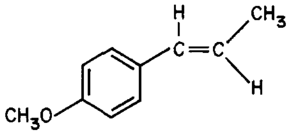
TABLE 1

Summary of Catalytic Efficiency[a]

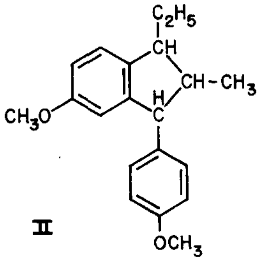
Catalyst	Percentage water initially present in catalyst	Percentage conversion of cyclohexylethanoate (±5%)
Al^{3+}—montmorillonite	14.8	98
Al^{3+}—montmorillonite (collapsed)	0	60
Cu^{2+}-montmorillonite	7.8	65
Cu^{2+}-montmorillonite (collapsed)	0	0
Co^{2+}-montmorillonite	8.0	75
Co^{2+}-montmorillonite (collapsed)	0	40
Fe^{2+}-montmorillonite	9.5	60
Ni^{2+}-montmorillonite	6.0	78
Na^{+}-montmorillonite	7.2	0
Cu^{2+}-'K10' (Süd Chemie acid-treated montmorillonite)	8.8	70
Cu^{2+}-Laponite XLG	6.5	40
Cu^{2+}-zeolite A	2.2	0
Cu^{2+}-zeolite 13X	10.0	20

[a] Conversion of cyclohexylethanoate after 7 hr reflux in xylene.

stances to yield metanethole (II) or isoanethole (III) and diisoeugenol (V), respectively (*7–12*).

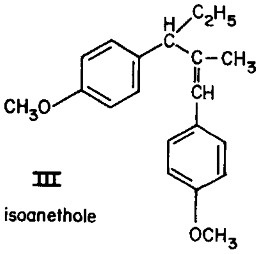


anethole I



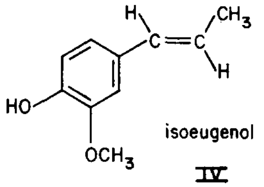
II

metanethole



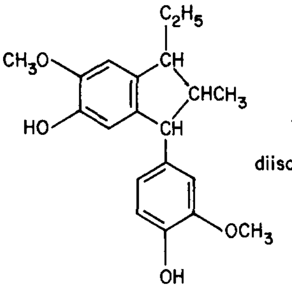
III

isoanethole



isoeugenol

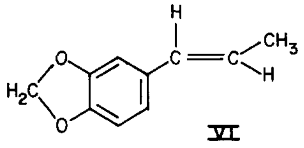
IV



V

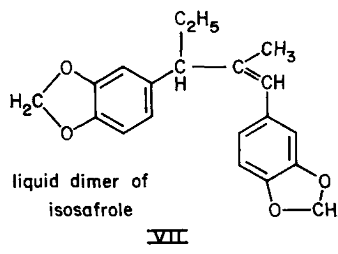
diisoeugenol

Three dimers of a third propenyl benzene, isosafrole (VI, 1-(3,4-methylene-dioxybenzene)-prop-1-ene) are known: two solid and one liquid. The liquid dimer was found to have a structure similar to isoanethole and the solid dimers were thought to be dimorphic or stereoisomeric forms of the indan structure (*13*). These solid dimers were thought to differ only in the configuration at the position 1 of the indan structure (*14*). The dimer of a fourth propenyl benzene, isohomogenol (XI,,1-(3,4-dimethoxybenzene)-prop-1-ene) was also found to possess the indan structure. Saturated dimers of other arylethylene derivatives are also known to be substituted phenylindans, e.g., dimeric styrene (*15*).



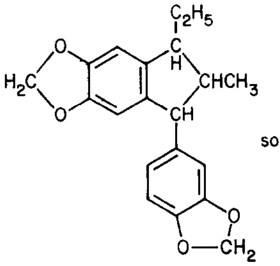
VI

isosafrole



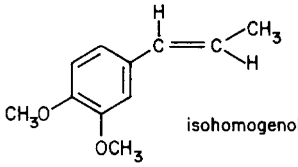
liquid dimer of isosafrole

VII

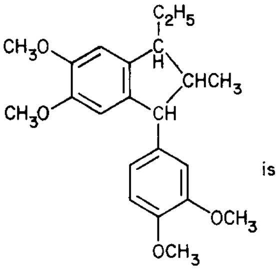


VIII

solid dimer of isosafrole



isohomogenol IX



X

dimer of isohomogenol

Until recently it was considered that the acid-catalyzed dimerizations of isohomogenol, isosafole, and anethole give principally the all *trans* (α)-racemates, with the minor products from isohomogenol and isosafrole being the 1,2-*cis*-2,3-*trans* (γ)-racemates. MacMillan *et al.* (*15*), from their ^{1}H NMR studies on the tricyclic dimers, assigned configurations which differed from those previously accepted.

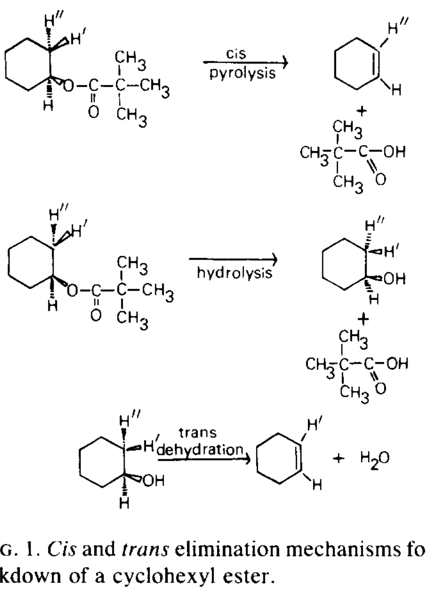


FIG. 1. *Cis* and *trans* elimination mechanisms for the breakdown of a cyclohexyl ester.

It is to be noted that the acid-induced dimerization of anethole leads to the all (γ)-racemate of metanethole while isohomogenol and isosafrole gave almost exclusively the 1,2-*cis*-2,3-*trans* (α)-racemates. A suggested mechanism for the tricyclic dimerizations is shown in Fig. 2.

A study of the dimerization of these monomers using clay catalysts appeared worthwhile not only because of the possibility of changing the proportions of different stereoisometric products compared with homogeneous reactions, but also because of the possibilities of attaining more facile conversions and hitherto unreported oligomers as has been found for other reactions catalyzed by clays (*1*).

The reaction procedure was to reflux 0.5 g of the cation-exchanged montmorillonite, 0.5 g of the appropriate propenyl benzene, and 10 cm^3 of solvent (typically octane). Where one of the reaction products was a

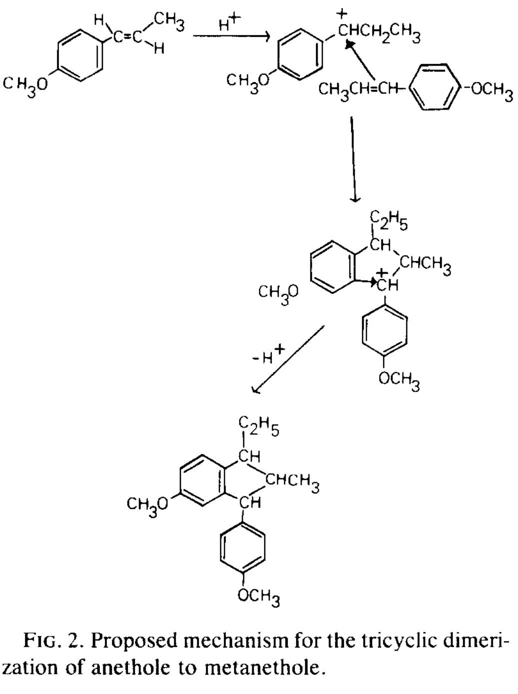


FIG. 2. Proposed mechanism for the tricyclic dimerization of anethole to metanethole.

solid, two experimental runs were made in parallel. The solid dimer was crystallized from one of the reaction mixtures and weighed; the remaining analysis was performed on the second reaction mixture using GLC (6 ft $\frac{1}{8}$" i.d. column packed with 3% OV1 silicone on Chromosorb G) and ^{1}H NMR.

a. Anethole (I). The liquid-phase, acid-catalyzed dimerization of anethole was performed initially to calibrate the analytical GLC; it was also noted that isoanethole was totally miscible in alcohol, whereas metanethole was only very slightly soluble, which provided a convenient method for separation of the isomers. A series of reactions using Al^{3+}-exchanged catalysts and different solvents was carried out to find a convenient reaction temperature for contact time of 1 hr. The weight of metanethole crystals produced depended upon the reflux temperature and was used as a crude measure of reaction efficiency: 0.0 g at 69°C (*n*-hexane), 0.167 g at 98°C (*n*-heptane), 0.284 g at 126°C (*n*-octane), 0.198 g at 138°C (xylene), and 0.206 g at 191°C (dekalin). The octane reflux temperature proved optimal and all further anethole dimerization runs were made with this solvent.

As in 1 above, a number of differently treated montmorillonites was used for the catalytic dimerizations (see Table 2). The acid-washed variety entailed using 1 mol dm^{-3} sulfuric acid into which the as-received bentonite was immersed for several hours. All the metal ion-exchanged montmorillonites, with the exception of the Na^+ variety, functioned as good catalysts, in line with the well-known Brønsted acidity of these particular cation-exchanged sheet silicates. Even the collapsed Al^{3+}-exchanged clay served as a reasonably efficient catalyst.

While the interlamellar cation in the silicate was not important so far as the fractional conversion of anethole was con-

TABLE 2

Comparison of Products of Reaction of Anethole with Various Cation-Exchanged Montmorillonites[a]

Cation-exchanged clay	Percentage anethol (I) conversion	Percentage metanethole (II) produced	Percentage metanethole (II) crystalized	Percentage isoanethole (III) produced	Dimers of unknown structure produced
Al^{3+}-montmorillonite	>95	52	32	48	48
Cu^{2+}-montmorillonite	>90	48	43	16	36
Ni^{2+}-montmorillonite	>95	58	44	27	15
Acid-washed montmorillonite	>90	60	—	23	17
Fe^{3+}-montmorillonite	>95	51	43	10	39
Co^{2+}-montmorillonite	>90	61	—	39	39
Na^{+}-montmorillonite	25	18	0	7	7
Collapsed Al^{3+}-montmorillonite	~43	24	36	19	19

[a] Reaction time 1 hr.

cerned, the interlamellar cation influenced the fraction of each dimer produced. Some montmorillonites brought about relatively clean reactions (e.g., Ni^{2+}–clay) in that a rather small number of different dimers were produced. Others, notably the Fe^{-3}-clay, gave a very high yield of mixture of dimers of unknown structure. The fraction of metanethole produced varied only slightly (except with the Na^+ and collapsed Al^{3+}–clays) and ranged from 48% (Cu^{2+}–clay) to 61% (Co^{2+}–clay). However, a real variation was seen between the percentage of isoanethole and the amount of dimers of unknown structure produced. Fe^{3+}–clay, for instance, gave only 10% isoanethole and 39% unknown dimers, whereas Ni^{2+}–clay produced 27% isoanethole and 15% unknown dimer.

The course of one reaction, catalyzed by Cu^{2+}–clay, was analyzed as a function of time. The original anethole produced metanethole, isoanethole, and other dimers. A further reaction was carried out in which a Cu^{2+}–clay was reacted with isoanethole in octane (Fig. 3). Here the isoanethole was broken up rapidly to form metanethole and the unknown dimers. These unknown dimers are, therefore, formed directly by dimerization of anethole as well as by isomerization of isoanethole.

To illustrate the preparative usefulness of the clay catalysts, we recall that the method of Baker and Enderby for the preparation of metanethole gave a maximum yield of 24% with a reaction time of 7 hr, whereas dimerization of anethole using a clay as an acid catalyst gave a recoverable yield of metanethole of 44% after only 1 hr.

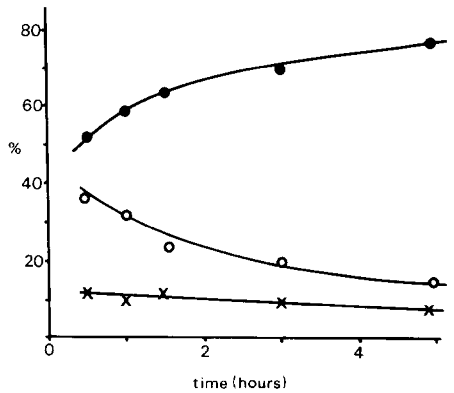


FIG. 3. Product distribution as a function of time for the reaction of isoanethole catalyzed by a Cu^{2+}–clay. ○, Isoanethole-linear dimer; ●, metanethole-tricyclic dimer; ×, unknown.

b. Isohomogenol (*IX*). With the same proportions of clay, reactant, and solvent as for the anethole experiments, with *n*-hexane (bp 69°C) used under reflux, it was found that Al^{3+}- and Fe^{3+}-exchanged montmorillonites were especially efficient catalysts. None of the other (divalent or monovalent ion-exchanged) montmorillonites listed in Table 2 was effective, there being no detectable conversion of isohomogenol after a 1 hr reflux. In contrast, the Al^{3+}- and Fe^{3+}-exchanged montmorillonites showed 43 and 30% conversion, respectively, under the same conditions. The collapsed Al^{3+}-montmorillonite as with the ester breakdown, again showed significant catalytic acidity. With the Al^{3+}-exchanged, expanded (uncollapsed) montmorillonite the percentage conversion increased linearly with time reaching ca. 60% after 5 hr. Complete conversion could be effected in shorter periods at higher temperature.

c. A Comparison of the dimerization behavior of anethole and isohomogenol. Notwithstanding their structural similarity (see formulas I and IX), these molecules exhibit distinctly different behavior in so far as catalytic dimerization is concerned. Both these species are intercalated (see d-spacing in Table 3) and in all cases the X-ray reflexions sharpened after reflux, signifying that ordering of the clay is enhanced following reaction of the monomer. But whereas both Al^{3+}- and Ni^{2+}-exchanged clays catalyze dimerization of anethole, only Al^{3+} is effective for the isohomogenol. There is no readily apparent reason why these differences occur: for the isohomogenol the Ni^{2+}- and Al^{3+}-exchanged clays which exhibit quite distinct behavior have essentially the same interlamellar spacing; and for the anethole there is comparable cataly-

TABLE 3

X-Ray Diffraction Data for Ion-Exchanged Clay Samples with Propenylbenzenes

	Al^{3+}-montmorillonite	Ni^{2+}-montmorillonite
Basal spacing of air-dried clay/Å	15.9	14.7
Basal spacing after reaction with anethole in octane/Å	15.2	13.4
Basal spacing after reaction with isohomogenol in hexane/Å	16.9	16.6

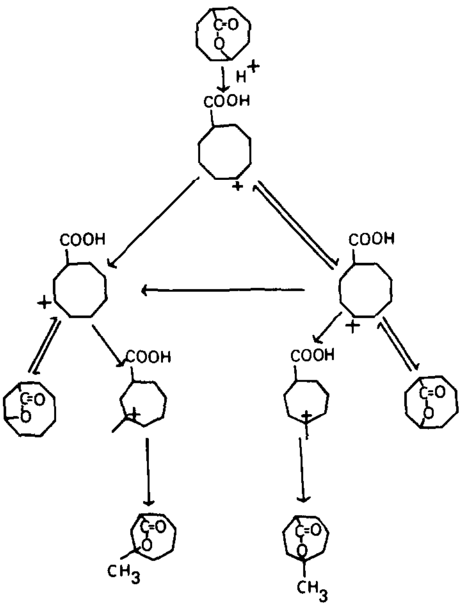


FIG. 4. Mechanism for production of carbolactones involving hydride shifts and ring contractions. After Cope *et al.* (*19*).

sis by both the Ni^{2+}- and Al^{3+}-bentonites, yet the interlamellar spacings are now quite different. There are obviously subtle changes in catalytic behavior brought about by the insertion of the extra methoxy group to anethole (to convert it to isohomogenol). This fact, along with the remarkable ease with which almost all of the ion-exchanged montmorillonite studied here catalyze the dimerization of anethole whereas only the very acidic montmorillonites (*16*) (Al^{3+}- and Fe^{3+}-exchanged) catalytically dimerize isohomogenol, merit further investigation, especially in regard to orientation, conformational mobility, and ease of protonation within the interlamellar spaces. In this connection it may be significant that the tricyclic dimer of isohomogenol formed in the clay-catalyzed reaction is the 1,2, *cis*-2,3-*trans*(α)-racemate whereas the tricyclic dimer of anethole is stereochemically distinct, i.e., the 1,2-*trans*-2,3-*trans*(α)-racemate.

3. *Lactonization of Cyclo-octene-5-carboxylic acid (XI)*

The acid-catalyzed lactonization of cyclooctene-5-carboxylic acid might be expected to give two lactones, 5-cyclo-oc-

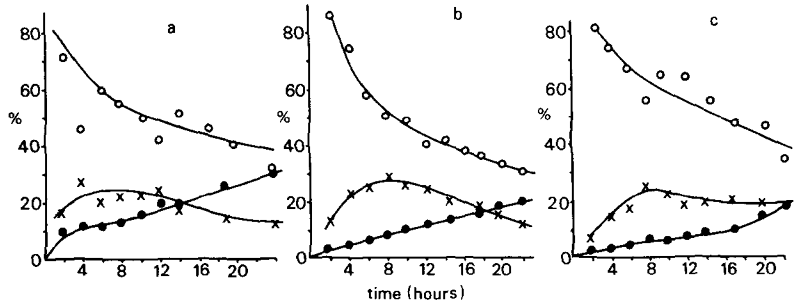
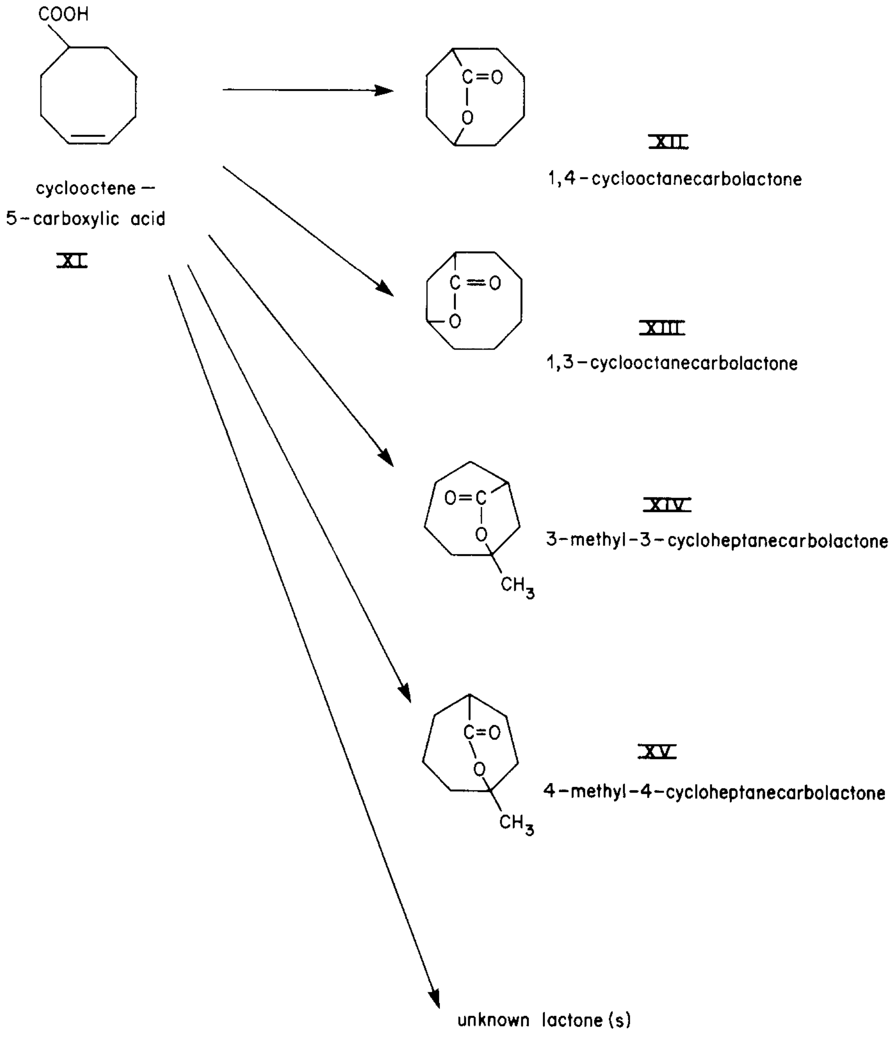


FIG. 5. Product distribution as a function of time for the reaction of cyclooctene-5-carboxylic acid over (a) Al^{3+}-montmorillonite, (b) Co^{2+}-montmorillonite, (c) Ni^{2+}-montmorillonite. ○, Cyclooctene-5-carboxylic acid; ×, 4-cyclooctanecarbolactone (XII); ●, 3-cyclooctanecarbolactone (XIII); XIV, XV, and unknown were produced in small amounts.

tene-carbolactone and 4-cyclo-octene-carbolactone. However five products are formed and all but one of these has been identified (*17–19*). It was found that the products from the rearrangement of 5-cyclo-octene-carbolactone under acidic conditions were the same as from lactonization of the acid. A mechanism involving direct hydride shifts (Fig. 4), rather than formation and subsequent hydration of an olefinic intermediate, was preferred because there was an absence of isolated olefinic products and because similar results were observed in the solvolysis of tosylates of methyl *cis*- and *trans*-hydroxycyclooctane carboxylate (*19, 20*).



cyclooctene — 5-carboxylic acid
XI

XII
1,4-cyclooctanecarbolactone

XIII
1,3-cyclooctanecarbolactone

XIV
3-methyl-3-cycloheptanecarbolactone

XV
4-methyl-4-cycloheptanecarbolactone

unknown lactone (s)

Dean (*17*) found that sulfuric acid was the only acidic reagent that caused lactonization of the cyclo-octene-5-carboxylic acid: concentrated hydrochloric acid, glacial acetic acid, formic acid, and trifluoroacetic acid were ineffective. The concentration of the sulfuric acid and the reaction temperature were found to affect the yield and ratios of the products formed.

Lactonization products, generated under homogeneous (liquid phase) conditions such as those described by Dean, were analyzed directly by GLC using a butanediol succinate column. Such a column was also used for the montmorillonite-catalyzed lactonizations. Unreacted acid gave rise to a GLC peak about coincident with that of 3-cyclooctane carbolactone. The acid could be removed with bicarbonate or converted to its methyl ester with diazomethane before analysis, the retention times of the methyl ester being different from that of any other product.

The most effective temperature of reaction was determined by varying the nature of the solvent in which the cyclooctane-5-carboxylic acid could be dissolved. The minimum effective temperature was found to be ca. 120°C (bp of *n*-octane).

There was facile conversion of the cyclooctene-5-carboxylic acid using Al^{3+}-, Fe^{3+}-, Co^{2+}-, Ni^{2+}-, and collapsed Al^{3+}-exchanged montmorillonite. With Cu^{2+}-exchanged montmorillonite only a small percentage of the acid was converted and, as with the ester breakdown with copper-exchanged zeolites 13X and 4A and sodium-exchanged montmorillonite, essentially no change occurred to the acid and for the same reasons as before. The reaction of collapsed Al^{3+}-montmorillonite with the acid was much slower than with hydrated Al^{3+}-montmorillonite. The products of the lactonization using cation exchanged montmorillonite were seen to be XII to XV and an unknown.

The reactions using Al^{3+}-, Co^{2+}-, and Ni^{2+}-montmorillonites were examined closely: analysis of products being by GLC. With Al^{3+}–clay the main reaction products were XII and XIII, the relative percentages of which were dependent upon reflux time (Fig. 5). Similar reactions using the 1,4-lactone (XII) and 1,3-lactone (XIII) as starting materials in place of the acid showed that XII gave a mixture of XIII, XIV, XV, and an unknown while XII gave XIII, XIV, and the unknown. The rates of reaction of the acid, the 1,4-lactone, and the 1,3-lactone were different in each case.

After reaction with the carboxylic acid, the basal spacing of an aluminium-exchanged bentonite was 14.5 Å and the (001) peak on the X-ray diffraction trace appeared sharp, whereas before reaction the basal spacing was 12.6 Å; this indicated that the acid had indeed been intercalated and it could not, therefore, be concluded that reaction was confined to the external surface of the catalyst. Assuming the lactonization of the acid took place both on the outer surface of the montmorillonite and between the clay sheets any lactone produced would have to compete with the acid for the active catalytic sites associated with the montmorillonite. With no acid present the reactions of the 1,4- and 1,3-lactones would naturally occur at a faster rate, a fact which explains why some 10 hr of refluxing is required, starting with cyclo-octene-5-carboxylic acid, for the consumption of the 1,4-lactone to be noticeable, whereas starting with 1,4-lactone, 50% conversion is seen after only 2 hr. The reaction of 1,4-lactone with Al^{3+}-montmorillonite, after approximately 6 hr, gave 55% yield of 1,3-lactone.

The rate of consumption of the olefinic acid with both Al^{3+}- and Co^{2+}-montmorillonite was similar, but the 1,4-lactone production was more rapid in the presence of cobalt montmorillonite (see Fig. 5).

Reactions with the 1,3- and 1,4-lactones showed that the isomerization was not as rapid over the Co^{2+}-exchanged catalyst as over an Al^{3+}-exchanged material. With Co^{2+}montmorillonite, as with Al^{3+}-montmorillonite, the 1,4-lactone was seen to isomerize initially to the 1,3-lactone and then the 1,3-lactone in turn isomerized to the other lactones.

The rate of consumption of cyclo-octene-5-carboxylic acid in the presence of Ni^{2+}-exchanged montmorillonite (Fig. 5) was seen to be similar to the rates seen with Al^{3+}- and Co^{2+}-montmorillonite. However this clay catalyst was unusual in that in reactions with the 1,3-lactone itself there appeared to be no isomerization to the other lactone products.

In summary, we find that certain cation-exchanged montmorillonites can act as acid catalysts for the lactonization of cyclo-octene-5-carboxylic acid; and that, initially, for the lactonization of the acid to 4-cyclooctane carbolactone, XII, the rate of consumption of the parent acid was similar with Al^{3+}-, Co^{2+}, or Ni^{2+}-montmorillonites. However the rates of isomerization of the lactones on the different exchanged montmorillonites differ appreciably, with the Al^{3+}-montmorillonite tending to be the best. All the reactions were time dependent: different reaction times produced different ratios of the products. The clay acid catalysts proved to be no better than the liquid phase catalysts in producing a high percentage of a particular lactone; but the clay-catalyzed reactions were time dependent and reaction was facile with 1,4- and 1,3-lactones (so that the use of the clay catalysts to produce these lactones in any substantial concentrations is not feasible). The clay catalysts may perhaps be used for the production of 4-methyl-4-cycloheptane (XV) carbolactone and 3-methyl-3-cycloheptane carbolactone (XIV), as these can be obtained in yields of up to 30% at suitable reaction times. Mechanistically, the proton addition step (see Fig. 4) again turns out to be crucial.

CONCLUSIONS

Ion-exchanged montmorillonites can act successfully as solid Brønsted acids in a range of organic reactions. The activity of the clay catalysts is high. For ester cracking it is found that high rates of decomposition can be achieved at 140°C compared with the 400°C necessary when cracking over pyrex or quartz surfaces. In the dimerization processes studied here, the reactions can be carried out at a relatively low temperature (130°C) and give rates of conversion greater than those obtained when following literature procedures using concentrated sulfuric acid as catalyst. The clay catalysts were also found to be as efficient for the lactonization reactions investigated as concentrated sulfuric acid.

In all of the reactions considered in this paper, and in earlier communications, one may rationalize the effectiveness of a particular cation-exchanged montmorillonite in terms of its known Brønsted activity (*16*).

ACKNOWLEDGMENT

We thank the SERC for support.

REFERENCES

1. (*a*) Adams, J. M., Ballantine, J. A., Graham, S. H., Laub, R. J., Purnell, J. H., Reid, P. I., Shaman, W. Y. M., and Thomas, J. M., *J. Catal.* **58,** 238 (1979): (*b*) Bylina, A., Adams, J. M., Graham, S. H., and Thomas, J. M., *J. Chem. Soc. Chem. Commun.* 1003 (1980); (*c*) Ballantine, J. A., Galvin, R. P., O'Neil, R. M., Purnell, J. H., Rayanakorn, M., and Thomas, J. M., *J. Chem. Soc. Chem. Commun.* 695 (1981): (*d*) Thomas, J. M., *in* "Intercalation Chemistry" (M. S. Whittingham and A. J. Jacobson, Eds.), pp. 55–99. Academic Press, New York, 1982.

2. Ballantine, J. A., Purnell, J. H., Rayanakorn, K., Thomas, J. M., and Williams, K. J., *J. Chem. Soc. Chem. Commun.* 9 (1981).

3. Ballantine, J. A., Davies, M., Purnell, J. H., Rayanakorn, M., Thomas, J. M., and Williams, K. J., *J. Chem. Soc. Chem. Commun.* 427 (1981).

4. Adams, J. M., Clement, D. E., and Graham, S. H., *Clays Clay Minerals* **30,** 129 (1982).

5. Ballantine, J. A., Davies, M., Purnell, J. H., Rayanakorn, M., Thomas, J. M., and Williams, K. J., *J. Chem. Soc. Chem. Commun.* 8 (1981).

6. Reid, P. I., Ph.D. Thesis, U.C.W., Aberystwyth, 1978.

7. Goodall, G. D., and Haworth, R. D., *J. Chem. Soc.* 2482 (1930).

8. Baker, W., and Enderby, J., *J. Chem. Soc.* 1094 (1940).

9. Muller, A., Mesaras, M., Kormendy, K., and Kussman, A., *J. Org. Chem.* **17,** 787 (1952).

10. Muller, A., *J. Org. Chem.* **12,** 815 (1947).

11. (*a*) Muller, A., *J. Org. Chem.* **16,** 481 (1951); (*b*) Muller, A., *J. Org. Chem.* **16,** 1003 (1951).

12. Haworth, R. D., and Mavin, C. R., *J. Chem. Soc.* 1363 (1931).

13. Baker, W., Godsell, J. A., McOmie, J. F. W., and Ullbright, T. L. V., *J. Chem. Soc.* 4058 (1953).

14. Cartwright, N. J., and Haworth, R. D., *J. Chem. Soc.* 948 (1947).

15. MacMillan, J., Martin, I. L., and Morris, D. J., *Tetrahedron* **25,** 905 (1969).

16. Mortland, M. M., and Raman, K. V., *Clays Clay Minerals* **16,** 393 (1968).

17. Dean, C. S., Ph.D. Thesis, U.C.W., Aberystwyth, 1966.

18. Jones, D. A., Ph.D. Thesis, U.C.W., Aberystwyth, 1968.

19. Cope, A. C., McIntosh, J., and McKervey, M. A., *J. Amer. Chem. Soc.* **89,** 4020 (1967).

20. Cope, A. C., and Nealy, D. L., *J. Amer. Chem. Soc.* **87,** 3122 (1965).