

REACTIONS OF THE CONJUGATED DIENES BUTADIENE AND ISOPRENE ALONE AND WITH METHANOL OVER ION-EXCHANGED MONTMORILLONITES

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Abstract—The reactions of simple conjugated dienes over divalent and trivalent transition metal-exchanged montmorillonites yield, in the absence of nucleophiles, a variety of products. Some of these products are a result of Diels-Alder cycloaddition reactions, whereas others are indicative of carbocation intermediates, i.e., other dimers, oligomers, and isomerization products of these intermediates. The reactions in sealed cells between 20° and 150°C show trends in the yields of the various product groups. Dimers of butadiene and isoprene formed by cycloaddition (i.e., 4-vinylcyclohexene and the monoterpene *p*-menthadiene (limonene)) were formed at low temperatures (20–50°C). As the temperature was raised, the total yield of dimers increased and higher oligomers were formed along with isomerization products of the dimers and oligomers. The products of cycloaddition, however, did not increase markedly. The type of solvent used for the reaction was found to influence the reactivity, e.g., the use of 1,4-dioxan rather than chloroform led to a reduction in total conversion and also to a markedly higher degree of selectivity. In the presence of a suitable nucleophile (methanol), both dienes gave the 1,4-addition product predominantly, which suggests that an allylic carbocation intermediate was involved. The use of an interlayer-supported nickel complex, $[\text{HNi}(\text{P}(\text{OEt})_3)_4]^+$, produced the only large scale polymerization observed in this work.

Key Words—Butadiene, Catalysis, Diels-Alder reaction, Gas-liquid chromatography, Isoprene, Methanol, Montmorillonite, Transition metal.

INTRODUCTION

Over the last few years interest in reactions of organic compounds catalyzed by supported reagents (McKillop and Young, 1979), such as ion-exchanged smectites, has grown. The reactions studied using such smectites have been diverse; the acid-catalyzed production of methyl *t*-butyl ether (MTBE, Adams *et al.*, 1981b, 1982b; Bylina *et al.*, 1980) and the hydrogenation of alkenes (Pinnavaia *et al.*, 1979) are typical examples. Different studies have tended to emphasize different features of these catalysts. Shape selectivity has been noted in some reactions (Adams *et al.*, 1981b; Pinnavaia *et al.*, 1979) and, although some products can be formed that are impossible to make by other routes (Adams *et al.*, 1978, 1979, 1982a) or are formed by reaction schemes that are unknown in other contexts (Ballantine *et al.*, 1981b), the common experience is that the reactions often take place under somewhat milder conditions than are usually employed (see, e.g., Adams *et al.*, 1982c; Ballantine *et al.*, 1981a).

The reactions of monoalkenes over acidic montmorillonite catalysts have been extensively studied, both alone and in the presence of nucleophiles, such as water and alcohols (Adams *et al.*, 1981a, 1983a, 1983b). These authors found that, with only one exception, the products of reaction below 100°C are derived from tertiary carbocation intermediates, whereas at higher temperatures secondary and primary carbocations can be involved. The reaction which does not fit these “rules”

is that of alk-1-enes, which react with the interlamellar water of montmorillonites to form di-2,2'-alkyl ethers (Adams *et al.*, 1979). Although this reaction proceeds below 100°C, a secondary carbocation is formally required to produce the ether.

In the present study the reactions of the simple conjugated dienes, butadiene and isoprene, both alone and with a typical nucleophile (methanol), have been investigated over various ion-exchanged montmorillonites. These materials are rather special alk-1-enes, and it was of interest to learn if they might also produce di-alkyl ethers at low temperatures. Moreover, these dienes can potentially give secondary, tertiary, and allylic carbocations. It was intended, therefore to study product distributions to see which carbocation intermediate predominated at different temperatures.

Dimerization and oligomerization reactions were expected because such reactions are well known for butadiene and isoprene. The Diels-Alder cyclization reactions leading to dimers are of particular industrial relevance: 4-vinylcyclohexene (VCH)—the cyclodimer of butadiene—can be converted to styrene by oxidative dehydrogenation, and the monoterpene products derived from isoprene cyclodimerization are important as flavorings and perfumes and in the pharmaceutical industry as precursors for a variety of products, notably vitamins (Meuly, 1972). These reactions are usually catalyzed by homogeneous systems using complexes of Ni, Fe, Co, or Pd (Maxwell, 1982). Recently, however,

a number of these homogeneous catalysts have been heterogenized (Scurrall, 1978) and, moreover, non-acidic silicate catalysts have proved to be efficacious (e.g., Cu⁺-exchanged zeolite Y (Reimlinger *et al.*, 1969), Cu⁺-montmorillonite (Downing *et al.*, 1978), and low-acidity, large-pore zeolites such as ZSM-20 or zeolite beta (Dessau, 1983)).

EXPERIMENTAL

Five types of modified clay catalysts were used in this study. Ni²⁺-, Co²⁺-, and Cr³⁺-montmorillonites were employed because they are known to be acidic catalysts; the Cr³⁺-exchanged samples are somewhat more acidic than the Ni²⁺- and Co²⁺-exchanged materials (see, e.g., Adams *et al.*, 1982b; Mortland, 1968). The fourth type of catalyst was a montmorillonite that contained a mixture of Ni²⁺ and Ag⁺ as exchangeable cations. This catalyst was expected to show some acidity (derived from the dissociation of clay interlamellar water by the Ni²⁺ ions); it should bind unsaturated hydrocarbons to the silver ions where reactions might take place. This type of interlayer interaction between the exchangeable cation and alkene reactant has been suggested as being important in other clay-catalyzed reactions (Adams *et al.*, 1981a; Pinnavaia *et al.*, 1979). Tolman (1972) demonstrated the activity of Ni(P(OEt)₃)₄ as a catalyst for isomerization and oligomerization. Because the active species was considered to be [HNi(P(OEt)₃)₄]⁺ (HNiTEP), which is cationic, a fifth type of catalyst was prepared by inserting this species between the layers of montmorillonite.

The <2- μ m fraction of the Wyoming bentonite used in this study (Volclay, foundry grade, Hopkin and Williams Ltd.) was obtained by sedimentation. Cr³⁺-, Ni²⁺-, and Co²⁺-exchanged clays were prepared by exposing the clay to 0.2 mole/liter solutions of Cr(NO₃)₃, NiCl₂, or Co(NO₃)₂ for 24 hr. The Ni²⁺/Ag⁺-clay was prepared by exposing the clay to a solution which was 0.2 mole/liter in both Ni(NO₃)₂ and AgNO₃. Some control reactions were carried out using Na⁺- and Al³⁺-clays, which were prepared from the respective chlorides by the same methods. The clay samples were then centrifuged and resuspended in deionized water repeatedly until a test of the supernatant for the exchanging salt proved negative. Thereafter the clays were isolated by centrifugation, dried in an oven at 40°C, ground finely, and maintained at a relative humidity (RH) of 12%. To prepare the HNiTEP-clay samples, the <2- μ m fraction of the montmorillonite was suspended in acidified (0.01 M HCl) methanol and treated with Ni(P(OEt)₃)₄, prepared after the method of Tolman (1972). The resulting samples were maintained in an atmosphere of 12% RH to produce the necessary acid environment in the clay interlayer region to stabilize the hydride.

The cation-exchange capacity (CEC) of this clay has been determined previously to be 70 \pm 2 meq/100 g of air-dry material (Adams *et al.*, 1983a) which

corresponds to $\frac{1}{6}$ Cr³⁺ or $\frac{1}{4}$ Ni²⁺ or $\frac{1}{4}$ Co²⁺ or $\frac{1}{2}$ [HNi(P(OEt)₃)₄]⁺ per Si₈O₂₀ unit. To obtain reproducible reactivity it was necessary to maintain the samples at constant RH to give fixed interlayer water contents because the acidity of the interlayer water is known to be a function of the amount of such water present (Mortland, 1968). Stainless steel reaction vessels were employed for all reactions involving butadiene. These containers were charged with 4 cm³ of liquid reagent (if necessary) and 0.5 g of the appropriate 12% RH clay. The cell was then cooled in liquid nitrogen, and 1 g of butadiene was admitted through a valve. After reaction, the cell was cooled to 10°C and opened. The contents were filtered and the liquid products were analyzed. For reactions involving isoprene, a Teflon-lined brass cell was used without a gas valve. A typical reaction involved 0.5–1.0 g of 12% RH clay together with 4 cm³ of each of the reactants and solvent. In all experiments the reaction vessels were placed in thermostatted oil-baths and stirred magnetically.

Gas-liquid chromatography (GLC) was used to analyze the reaction products. The column employed was 2.7 m of 4-mm i.d. glass filled with 3% polyethylene glycol 20 M with 10% silver nitrate, supported on Chromosorb G. When nuclear magnetic resonance (NMR) studies of products were required, a preparative GLC column with 8-mm internal diameter was employed. Samples of the chosen products were collected under carbon tetrachloride. Additional evidence for the identification of products was supplied by the use of (KRATOS MS25) GLC mass spectroscopy (see Budzikiewicz *et al.*, 1964; Ryhage and von Sydow, 1963; Thomas and Willhalm, 1964).

RESULTS

Reactions of butadiene

Using a Cr³⁺-montmorillonite catalyst at temperatures as high as \sim 60°C, some VCH—the butadiene cyclo dimer—was formed as the sole observable product. At higher temperatures the yield of 4-vinylcyclohexene increased and a complex mixture of higher oligomers was also produced. The clay turned black during the higher temperature reactions. The appearance of the clay was suggestive of coke formation, as has been observed for many systems (see, e.g., Eisenbach and Gallei, 1979).

Reactions of butadiene with methanol

Control reactions using no clay catalyst at room temperature produced only a small amount of VCH. At 130°C, on the other hand, a rubber, a small amount of (liquid) 1-methoxybut-2-ene, some cracking and isomerization products, and some mixed oligomers were produced.

When a Cr³⁺-montmorillonite catalyst was used between 20° and 150°C (Table 1), very few products were

Table 1. Typical results for the reactions of butadiene with methanol over Cr³⁺-montmorillonite (4-hr reaction).

Temperature (°C)	Conversion of butadiene (%)	4-vinyl cyclohexene	Products ¹			
			C ₆ products	1-methoxy but-2-ene (1,4-product)	3-methoxy but-1-ene (1,2-product)	Unidentified products (mostly oligomers)
60 ²	56	52	0.5	2.0	0.8	1
100	63	52	1.6	3.7	2.1	3
150	76	45	0	5.0	3.0	23

¹ Yields are expressed in terms of % conversion of butadiene (or isoprene) to each of the products.

² Note that at 60°C use of 98% H₂SO₄ gave ~5% conversion of butadiene after 4 hr.

formed at the lower temperature (~1% of the total GLC sample envelope) apart from some VCH. The principal liquid products formed between 80° and 100°C were 1-methoxybut-2-ene, a C₆ mixture (probably of cyclohexene and methylcyclopentene), and VCH. At >100°C dimerization increased rapidly, so that in addition to larger yields of the above products, higher molecular weight species were also formed. These products gave clearly defined and well-separated GLC envelopes and did not show the large scale polymerization seen in the absence of a clay catalyst (see Figure 1).

At higher temperatures the higher molecular weight products were sufficiently abundant to cause a separation of the liquid product into two fractions; one fraction was essentially methanol saturated with an alkene/alkane mixture, and the other was a brightly colored (orange-yellow) viscous oil. At all temperatures it was necessary to vent off gas before sampling the liquid products. This gaseous phase was analyzed and shown to be primarily butadiene. The appearance of C₆ species in the product suggests that some cracking of higher molecular weight species took place. Although the analytical technique did not allow their detection, ethylene or ethane may also have been a component of the gaseous fraction.

When a Ni²⁺-montmorillonite catalyst was used the products reflected a much weaker acid environment than that of the Cr³⁺-exchanged catalyst. The products were essentially the same, but the reaction gave a lower yield and fewer dimerization and oligomerization envelopes.

When a HNiTEP-clay catalyst was used at low temperatures, product yields were very low, typically ~1% of the total butadiene present, but at higher temperatures a rubber product was formed. At 180°C the contents of the reaction cell were a hard rubber-clay matrix containing a liquid that effervesced rapidly, indicating a low boiling point component. A methanol washing of the cell contents revealed only butadiene, methanol, and VCH, but the gaseous product was probably not merely excess butadiene, because, despite cooling to

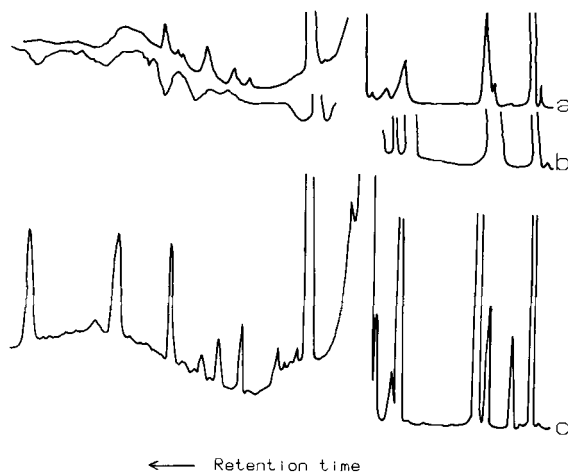


Figure 1. Gas-liquid chromatograph trace of the product mixtures from the reaction between 1,3 butadiene and methanol over (a) no catalyst, (b) 98% H₂SO₄, (c) Cr³⁺-montmorillonite. The product distribution varies considerably with different catalysts.

<0°C, it still boiled away rapidly. In view of this observation, one of the gaseous products might have been dimethylether (see Adams *et al.*, 1982b).

Because the clay catalysts behaved in many ways like 'solid acids,' a brief study was made of the reaction of butadiene with methanol over 98% sulfuric acid. Below 100°C, the GLC product trace was similar to that found for the clay catalyzed reactions, but it indicated much lower yields of dimer and almost as much 1-methoxybut-2-ene. At higher temperatures, reproducible results were difficult to obtain, but cracking and isomerization products were present in addition to higher molecular weight products than were formed when clay catalysts were used (see Figure 1).

Reactions of isoprene

The isoprene used in this study contained a small amount (0.8% by weight) of limonene, probably a product of a Diels-Alder-type concerted reaction of two isoprene molecules. When isoprene alone was heated at 60°C in a reaction vessel no significant new products were formed. In the presence of Cr³⁺-montmorillonite, however, at 60°C in a sealed cell or under reflux conditions (~65°C), some monoterpene products were formed. In order of appearance from the GLC column, these were limonene, β-ocimene X, and an unknown (characterized by an unusually high m/e peak at 73, but otherwise similar to α-fenchene), and camphene. These materials are C₁₀H₁₆ species and are found naturally in the 'essential oils' of some plants. After 4 hr the total yields were 10% of the initial isoprene for reactions in sealed cells, but only 1% for reaction under reflux. At higher temperatures greater conversions were achieved and at 120°C the product was an oil which was rich in C₁₀H₁₄, C₁₀H₁₆, C₁₀H₁₈, C₁₀H₂₀, C₉H₁₈,

Table 2. Reactions of isoprene and methanol over Cr³⁺-montmorillonite catalyst (4-hr reaction).

Temperature (°C)	Conversion of isoprene (%)	Products ¹				
		C ₁₀ H ₁₆ (% limonene in parentheses)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{OCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}=\text{CH}-\text{CH}_2-\text{OCH}_3 \end{array}$	C ₁₀ H ₁₇ OCH ₃	Material with >C ₁₀
20	3.8	3.8 (3.0)	—	—	—	—
60	22	4.8 (2.5)	4.9	12.3	—	—
90	67	24.5 (6.0)	10.1	22.9	8.3	1.2
120	93	49.6	0.8	1.4	34.8	6.4

¹ Yields are expressed in terms of % conversion of butadiene (or isoprene) to each of the products.

C₉H₂₀, C₉H₁₆, and higher oligomers. In addition, some trimeric products evidently formed together with some alcohols and ethers suggestive of reaction between isoprene and clay interlayer water. The single most abundant species was shown to be 4-ethyl-o-xylene (C₁₀H₁₄). The total conversion of isoprene was ~90% at these temperatures, but the reaction was very unselective. More than 20 product envelopes were apparent on GLC traces. They included no species of C₂₀ or greater which were certainly present, as evidenced by the viscosity of the product. Thus, the 4-ethyl-o-xylene did not exceed 10% of the total isoprene reacted. In the absence of the Cr³⁺-montmorillonite catalyst, the isoprene did not react to any significant extent; neither did it do so when heated over CrCl₃.

Adams *et al.* (1983b) noted that the choice of solvents markedly affects the reaction products and yields in clay-catalyzed reactions. To investigate such effects here, a study was made of the reaction of isoprene over Cr³⁺-montmorillonite using the solvents chloroform and dioxan. In reactions with chloroform, the products were similar to those when no solvent was used. In marked contrast, the use of 1,4-dioxan significantly altered the product distribution. The total conversion of isoprene was reduced considerably as was the range of product types. Significantly, it was the high molecular weight products that no longer formed.

Reactions of isoprene and methanol

A study of the reaction of isoprene and methanol was carried out between 20° and 120°C in the presence of Cr³⁺-montmorillonite (see Table 2). At 20°C, ~4% conversion was noted after 4 hr. The yields increased markedly with increasing temperature; at 60°C, 30 separable products were found on the GLC trace. At 80°C, the yield of monoterpenes was at a maximum, and at 100° and 120°C the variety of products increased again and the products were biphasic. One clear phase was essentially methanol saturated with products that were also present in the extremely viscous and dense lower yellow phase. These products were oils which were high molecular weight unsaturated oligomers of isoprene and ether and alcohols that were formed by the nucleophilic attack on the carbocations found in the pres-

ence of the acid clay. A typical GLC trace of the product at 80°C is shown in Figure 2; the peaks are identified in Table 4.

When other ion-exchanged montmorillonites were used as catalysts for this reaction the rate of conversion of the reactant changed markedly as did the yield of the different products. For example, when a Ni²⁺/Ag⁺-clay or a Co²⁺-clay was used, the number of products was reduced; the only product of significance was limonene (Table 3). The use of certain solvents markedly affected the results as well. When isoprene was reacted with methanol in chloroform (b.p. 62°C) or heptane (b.p. 97°C) under reflux conditions the clay catalyst turned orange immediately after the addition of isoprene. When heptane was used, no new products were formed, and the yields of ethers were less than those for reactions at similar temperatures in a cell with no solvent. Moreover, no oligomers having a molecular weight greater than limonene were formed, and no evidence of limonene isomerization was found. The use of chloroform as a solvent gave products and yields similar to those found for no solvents.

Some comparison reactions were carried out at 90°C using Na⁺- and Al³⁺-clays. The Na⁺-clay gave almost

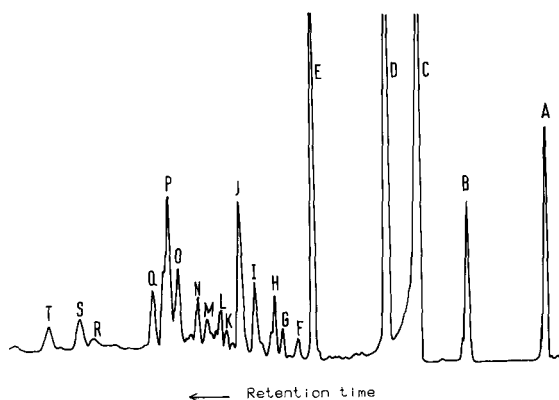


Figure 2. Gas-liquid chromatograph trace of product distribution from reaction of isoprene and methanol over Cr³⁺-montmorillonite at 80°C. Identification of peaks is made in Table 3.

Table 3. Reactions of isoprene and methanol over a range of ion-exchanged montmorillonite catalysts (4-hr reaction, 90°C).

Exchangeable cation	Conversion of isoprene (%)	C ₁₀ H ₁₆ (% limonene in parentheses)	Products ¹			
			$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{OCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}=\text{CH}-\text{CH}_2-\text{OCH}_3 \end{array}$	C ₁₀ H ₁₇ OCH ₃	Material with >C ₁₀
Cr ³⁺	67	24.5 (6.0)	10.1	22.9	8.3	1.2
Co ²⁺	5.4	5.4 (4.8)	—	—	—	—
Ni ²⁺ /Ag ⁺	9.5	6.6 (5.4)	1.8	1.1	—	—

¹ Yields are expressed in terms of % conversion of butadiene (or isoprene) to each of the products.

no products, whereas the Al³⁺-clay gave high yields of methoxy ether derivatives of isoprene, without dimerization products.

DISCUSSION

Butadiene reactions

The experimental data show that as the temperature was raised, the clay catalysts exhibited an increasing range of catalytic abilities. At less than about 80°C, VCH was essentially the sole product. The Ni²⁺- or Cr³⁺-montmorillonites acted as a Diels-Alder dimerization catalyst, the efficiency of which was not related to the undoubted Bronsted acidity of the silicate, because if free carbocations were involved in the reaction, methanol would have trapped them before they could have reacted further to give VCH. Between 80° and 100°C the efficiency of the Diels-Alder catalysis increased, i.e., contributed to yield of VCH, but a significant amount of 1-methoxybut-2-ene was also produced. Production of this methoxy ether was the first

evidence of acid catalysis. Because this ether is a result of 1,4-addition to the butadiene, its production implies the existence of an allylic carbocation intermediate which had been attacked by methanol. At these temperatures also, some C₆ products were formed that were the result of acid-catalyzed cracking reactions. As the temperature was raised, even more products formed which were derived from secondary and primary carbocations.

Isoprene reactions

The general pattern of activity noted was similar to that found for butadiene, i.e., dimerization occurred at low temperatures (20°–60°C) and increased with temperature, whereas competing reactions, such as attack by nucleophiles and oligomerization, became apparent and increased as the temperature was raised. These products contrast markedly with those produced by butadiene reactions because the dimers formed were not all the result of Diels-Alder cycloadditions. As the acidity of the clay interlayer region increased (Co²⁺ ≈

Table 4. Identification of gas-liquid chromatographic peaks in Figure 2 by mass spectrometry.¹

Product peak	Empirical formula	Identification of products ²	
A	C ₅ H ₈	CH ₂ =C(CH ₃)CH=CH ₂	Isoprene
B	C ₆ H ₁₂ O	(CH ₃) ₂ C(OCH ₃)CH=CH ₂	1,2 addition product of MeOH to isoprene
C	CH ₃ OH	CH ₃ OH	Methanol
D	C ₆ H ₁₂ O	CH ₃ -C(CH ₃)=CHCH ₂ OCH ₃	1,4 addition product of MeOH to isoprene
E	C ₆ H ₁₄ O ₂	(CH ₃) ₂ C(OCH ₃)CH(OH)CH ₃	Addition product of water to component B
F	—	—	—
G	C ₁₀ H ₁₆	} Monoterpenes	Limonene
H	C ₁₀ H ₁₆		l-terpinolene
I	C ₁₀ H ₁₆		α-terpene
J	C ₁₀ H ₁₆ OH	} Alcohols of monoterpenes	Possibly carveol
K	C ₁₀ H ₁₆ OH		Possibly geraniol
L	C ₁₀ H ₁₆ OH		Possibly tetrahydrolinalool
M	C ₁₀ H ₁₆ OH		Possibly lavandulol
N	C ₁₀ H ₁₇ OCH ₃	} Methoxyethers of monoterpenes	—
O	C ₁₀ H ₁₇ OCH ₃		—
P	C ₁₀ H ₁₇ OCH ₃		—
Q	—	} Higher terpenes and cracking/isomerization products	—
R	—		—
S	—		—
T	—		—

¹ The reaction is that of isoprene and methanol over a Cr³⁺-montmorillonite at 80°C.

² It was not possible to identify *all* of the products unambiguously.

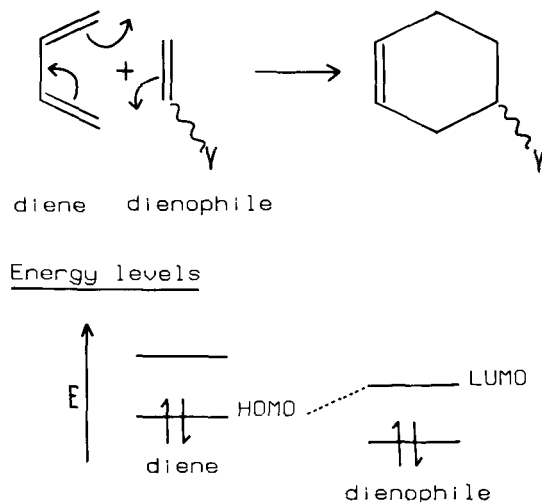


Figure 3. Mechanism and energy levels for a Diels-Alder cycloaddition reaction.

$\text{Ni}^{2+}, \text{Ag}^+ < \text{Cr}^{3+}$), the Diels-Alder dimerization efficiency remained constant, whereas the total dimerization efficiency increased 4-fold. The differences found here derive from the fact that isoprene is capable of forming a tertiary carbocation upon protonation. Adams *et al.* (1983b) showed that reactions involving such intermediates (but not secondary or primary carbocations) can occur below 100°C over montmorillonite catalysts. The tertiary carbocations formed here from isoprene were attacked by other alkenes to give dimers. This latter reaction has a completely different mechanism than that of a Diels-Alder dimerization and gave different dimer products.

Although, hypothetically, mono-terpenes can be formed from the hemiterpene isoprene, under actual acid conditions the synthesis is not straightforward (Meuly 1972) and usually not selective. In the present study, a fairly clean conversion of isoprene to mono-

terpenoid chemicals was noted, however, only at $<100^\circ\text{C}$. At $>100^\circ\text{C}$ the yield increased markedly, but chromatographic studies showed numerous product envelopes and that separation was extremely difficult. The fact that these products appeared under the highly acid conditions present in the interlayer of a trivalent-cation-exchanged clay suggests that they must have been highly stable in the interlayer environment. As was suggested by Adams *et al.* (1982a), some conformation preference may have shielded the species involved from further proton (or nucleophile) attack.

Many of the products of these reactions are likely to have been derived from limonene by isomerization, etc. Frenkel and Heller-Kallai (1983) showed that the products formed by the reaction of limonene over different ion-exchanged montmorillonites are functions of the interlayer cation.

Mechanistic considerations

The formation of acid-catalyzed reaction products of the dienes employed here was not unexpected. Until very recently, however, montmorillonites have not been recognized as Diels-Alder catalysts except for oleic acid dimerization (den Otter, 1970a, 1970b, 1970c), and with reference to his work the clay probably isomerizes the acid to produce a pair of conjugated double bonds and to transfer hydrogen from one molecule to another. These reactions are usually carried out industrially at $\sim 230^\circ\text{C}$, and at this temperature thermal Diels-Alder activity is expected. Moreover, although Cu^+ -montmorillonite is known to dimerize butadiene (Downing *et al.*, 1978), the clay is only a support for the Cu^+ ions and the reaction is thought to proceed via a bis- π -allyl complex which is only likely for Cu^+ or Ni^0 .

Diels-Alder cycloadditions are concerted reactions involving the highest occupied molecular orbital of a diene and the lowest unoccupied molecular orbital of a dienophile (Morrison and Boyd, 1973; Figure 3). To obtain high reaction rates, the energies of these two orbitals must be comparable. This situation is com-

Table 5. Summary of reaction products using Cr^{3+} -montmorillonite catalysts.

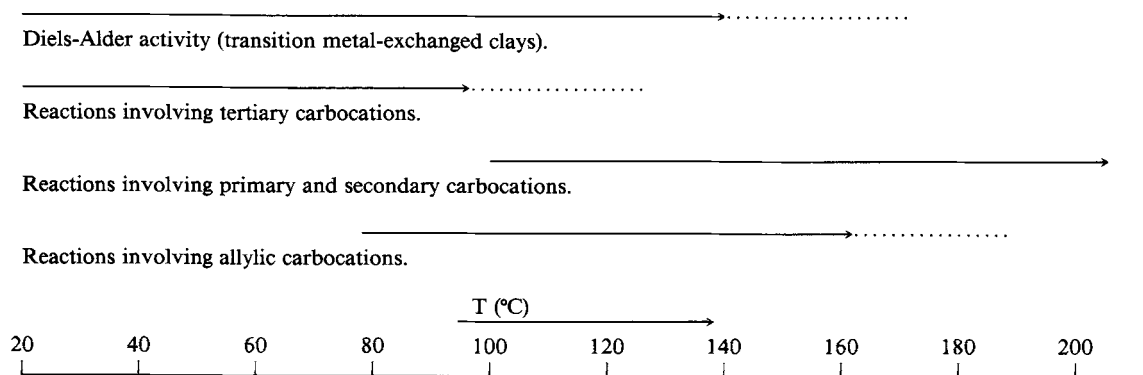
Reactants	Temperature ($^\circ\text{C}$)	Products
Butadiene	20	4-vinylcyclohexene
	60	
	100	
Butadiene + methanol	20	4-vinylcyclohexene and oligomers of butadiene
	60	
	100	
Isoprene	20	Limonene
	60	
	100	
	>100	
Isoprene + methanol	20	Limonene, monoterpenes, and oligomers of isoprene
	60	
	100	
		Major product is p-cymene ($\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CH}_3)_2$)
		Methoxy ethers of isoprene, limonene, and monoterpenes, alcohols and methoxy ethers of monoterpenes with higher molecular weight oligomers

monly achieved by the presence of an electron-withdrawing substituent on the dienophile and by using Lewis acids that can complex with oxygen functions on the dienophile. Laszlo and Lucchetti (1984b) showed that Fe³⁺-exchanged K10 (a commercial acid-treated bentonite, produced by Süd-Chemie AG, Munich) can act as a Lewis acid catalyst for Diels-Alder reactions involving such substituted dienophiles.

For the reactions of unactivated hydrocarbons, Bellville and Bauld (1981, 1982) showed dramatically increased activity using a radical-cation catalyst. Laszlo and Lucchetti (1984a) successfully used a mixture of 4-t-butylphenol (which readily forms radical cations) and Fe³⁺-K10 as a Diels-Alder catalyst. They noted that Zn²⁺-, Co²⁺-, or Al³⁺-exchanged K10 gave inferior results. Fe³⁺-K10 alone gave yields of ~60% of those achieved when it was used in conjunction with the

phenol. In the present work, the Diels-Alder activity of the clay catalysts was most likely due to the formation of radical cations which involved the interlayer cation (or, just possibly, the Fe³⁺ present in the clay layers) in a one-electron transfer. The direct involvement of the interlayer cation can be inferred from the change in color noted upon interaction of the clay with the diene. Moreover, a Lewis-acid-type activation is unlikely without an oxygenated substituent on the dienophile. Indeed, the control experiments using Al³⁺-clays gave no Diels-Alder cyclodimerization products.

From the present data and those reported by Adams *et al.* (1983a, 1983b) and Ballantine *et al.* (1981a, 1982b), the following schematic summary of the catalytic activity of ion-exchanged montmorillonites towards alkenes can be made:



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