JOURNAL OF CATALYSIS 95, 300–304 (1985)

Hole-Catalyzed and Photoassisted Hole-Catalyzed Pericyclic Reactions on Zeolites

The initial observations of single electron acceptor (hole) catalysis of cycloaddition reactions by zeolites are reported. Both spontaneous and photoassisted zeolite hole catalyses are observed for several conjugated organic substrates including dienes and styrenes. The zeolite hole catalyst sites are characterized as very mild in comparison to aminium salt hole catalysts and are subject to competition from Brønsted acid-catalyzed processes in some cases. © 1985 Academic Press, Inc.

INTRODUCTION

Catalysis of the Diels–Alder reaction by single electron acceptor (hole) catalysts has been shown to provide a powerful and highly selective format for the cycloaddition of neutral or electron-rich dienophiles to conjugated dienes (*1–5*). The propagation cycle of the cation radical mechanism proposed for these reactions (Scheme 1) consists of a pericyclic step, which involves the cycloaddition of a cation radical to a neutral species, and an electron transfer step, which neutralizes the cation radical cycloadduct and generates more chain-carrying cation radicals. The enormously enhanced rates of cycloaddition of cation radicals to neutrals, relative to the corresponding cycloaddition of two neutral molecules, make possible catalytic factors of 10^{18} or greater (*5*). Zeolites (molecular sieves) are among the most widely used and important catalysts in the chemical industry as a consequence, partly, of their shape selectivity but also as a result of their exceptional Brønsted acidity (*6*). Zeolites are also known to posses distinct Lewis acid sites at which ionization of neutral substrates to cation radicals (especially aromatic cation radicals) can occur (*7–9*). This communication reports the first observations of the ability of zeolites to function as hole catalysts for pericyclic reactions. Analogous hole catalysis on doped montmorillonite clay has been observed in very recent work (*10*).

METHODS

A variety of conjugated dienes and styrenes was stirred with a zeolite suspended in dichloromethane solution, at room temperature or with refluxing, for various periods of time. Zeolites of the 13X, 5A, and 4A types (for convenience, beads or extrudate pellets were preferred) were obtained from Aldrich and used directly. The results with the wide-pore (13X) sieves were far superior and are emphasized in this paper. Although used less extensively in this work, a clinoptilolite zeolite (Zeolon 400; 1/16-in-pellets) donated by the Norton Company proved equally as effective for hole-catalysis. The dienes and styrenes were obtained from Aldrich and, in a few cases, were donated (*10*). These included 1,3-cyclohexadiene, 1-methyl-1,3-cyclohexadiene, 1,1′-dicyclopentenyl, 2,4-dimethyl-1,3-pentadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, *t,t*-2,4-hexadiene, *t*-anethole, and β-methylstyrene. Reactions were monitored by GC and analyzed by GC/MS. In those cases where reactions

$$\mathrm{DP} \xrightarrow{\mathrm{H}} \mathrm{DP}^{+\cdot} \qquad \text{Initiation}$$

$$\left.\begin{array}{l}\mathrm{DP}^{+\cdot} + \mathrm{DN} \longrightarrow \mathrm{A}^{+\cdot}\\ \mathrm{A}^{+\cdot} + \mathrm{DP} \longrightarrow \mathrm{A} + \mathrm{DP}^{+\cdot}\end{array}\right. \qquad \text{Propagation}$$

DP = dienophile
DN = diene
A = adduct
H = Hole catalyst

SCHEME 1

0021-9517/85 $3.00

proceeded reasonably efficiently, products were isolated (preparative GC and/or distillation) and characterized by PMR and CMR spectroscopy. In the photoassisted reactions, a Hanovia 450-W medium-pressure mercury lamp fitted with a Pyrex filter was used. Parallel blank reactions omitting the zeolites were run in every case. Small-scale runs, appropriate for GC yields and GC/MS analysis, utilized 2–3 g of zeolite suspended in 5–7 ml dry dichloromethane as the catalyst/solvent system for dimerization of 50–60 mg of the organic substrate. The zeolites were washed with several 5-ml volumes of dichloromethane after the desired reaction duration and the extracts evaporated on a rotary evaporator. Weighed amounts of biphenyl were also included as an internal standard in runs used to determine GC yields. Preparative runs on scales 5 to 10 times this size were carried out for product isolation.

RESULTS

When 1,3-cyclohexadiene (**1**, 0.088 g, 1.1 mmol) was stirred in dichloromethane solution (6 ml) with Linde 13X molecular sieves (2.63 g) for 24 h at reflux (bp 40°C), a 13% conversion to the *endo* and *exo* Diels–Alder cyclodimers **2** and **3** (3.8 : 1) was achieved. With 5A sieves the conversion achieved was just 6%. No dimers other than **2** and **3** (such as the cyclobutane dimers **4** and **5**) were formed in these reactions, and neither were significant amounts of trimers formed. Vapor-phase reaction of **1** over 13X sieves at 100°C, instead of improving the conversion led to decomposition of **1** without formation of cycloaddition products.

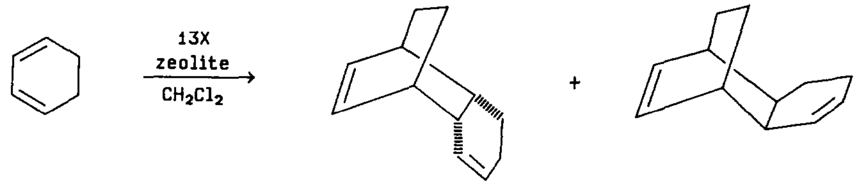
Photoassisted hole-catalyzed Diels–Alder cyclodimerization of **1** was more efficient than the purely thermal catalytic process. Irradiation of the zeolite/dichloromethane/**1** mixtures using a Pyrex filter to absorb higher energy UV light (at ambient temperature) led to **2** and **3** in 37% yield after only 5 h (13X sieves). Control runs omitting the sieves revealed the formation of mixtures of **2–5**, but primarily of the cyclobutanes **4** and **5**, which arise from triplet **1** (*12*). 1-Methyl-1,3-cyclohexadiene was subject to a similar photoassisted zeolite-catalyzed dimerization giving the two Diels–Alder dimers previously reported (23% conversion in 7 h) (*2*). Acyclic dienes, which lack the relatively long wavelength (259 nm) absorption of **1**, were not subject to photoassistance. The nonphotoassisted zeolite-catalyzed dimerizations of such dienes (see Methods for an inventory of dienes investigated) were, unfortunately, even less efficient than that of **1**.

Zeolite catalysis of a [2 + 2] olefin cycloaddition was also observed in the specific case of the highly electron-rich substrate *trans*-anethole (**6**). Yields of dimers up to 46% were obtained after 48 h of nonphotassisted reaction (stirring at reflux with 13X sieves). The dimer mixture contained three components, one of which (55%) was the well-known *trans,anti,trans*-cyclobutane dimer **7**, resulting from hole-catalyzed dimerization (*13*). The other two dimers (45%; unidentified) were noncyclic and appeared to emanate from a competing Brønsted acid-catalyzed reaction. β-Methylstyrene was dimerized analogously, but much less efficiently (<5% conversion) using the photoassisted process.

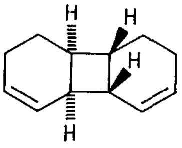
In the presence of 13X molecular sieves, in only 2 h (without photoassistance), 2,4-dimethyl-1,3-pentadiene (**8**) was smoothly dimerized (90%) to **9**. This dimerization, in contrast to the previous ones, is apparently not a hole-catalyzed process, since the dimer of **8** obtained via hole catalysis is **10** (*14*). Indeed, conventional Brønsted acids (HBr, $HSbCl_6$) have been shown to dimerize **8** to **9**.

DISCUSSION

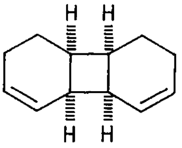
The uncatalyzed thermal Diels–Alder dimerization of 1,3-cyclohexadiene (**1**) requires heating at 200–250°C for a period of 2 days and then affords only a 30% yield of **3** and **4** (4 : 1 ratio) (*1*). The dimerization of



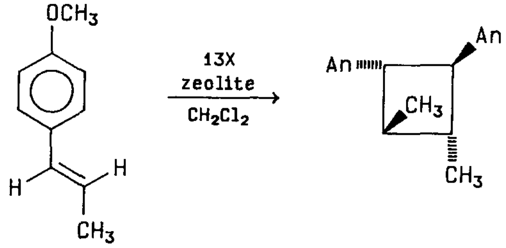
1 **2** (*endo*) **3** (*exo*)



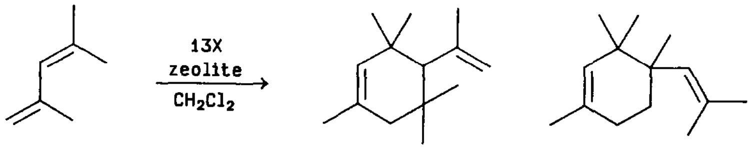
4 (*anti*)



5 (*syn*)



6 **7**
(An = *p*-methoxyphenyl)



8 **9** **10**

1 is not subject to catalysis by even strong Brønsted acids. In contrast, catalytic quantities (3–5 mol %) of the hole catalyst *tris*-(*p*-bromophenyl) aminium hexachlorostibnate [or larger quantities of a cation radical polymer (CRP)] in dichloromethane solvent at 0°C effect the dimerization of **1** in 70% yield within 5 min (**3** : **4** = 5 : 1). Catalysis of this same pericyclic reaction by 13X and clinoptilolite zeolites, although proceeding rather slowly, provides the first instance in which hole catalysis on zeolites has been observed. The exclusive formation of Diels–Alder adducts (**2** and **3**) in the characteristic ratio 4 : 1 is typical of the hole-catalyzed dimerization of **2**. The still slower hole-catalyzed dimerization of **1** on small-pore zeolites (5A, 4A) suggests the possibility that some, but clearly not all, dimerization occurs within the pores of the 13X sieves. In contrast, the Brønsted acid-catalyzed dimerization of 2,4-dimethyl-1,3-pentadiene (**8**) proceeds essentially equally efficiently on 13X and 5A sieves and but very little less efficiently on 4A sieves. All of the substrates in this study are too large to be absorbed in the relatively small pores of the 5A and 4A zeolites. The hole catalytic sites in the zeolites are further characterized as quite mild in comparison to the aminium salt catalyst, since the dimerization rates are enormously greater for the latter catalyst.

The photoassisted zeolite-catalyzed dimerization of **1** evidently occurs via excited state (presumably triplet) **1**. Electron transfer to the zeolite sites is obviously much more facile from such excited states than from the ground state. Small amounts (5–15%, depending on the reaction scale and irradiation time) of the cyclobutane dimers associated with addition of triplet **1** to ground state **1** accompany the formation of the Diels–Alder dimers and give evidence of the intermediacy of triplet **1**. A consequence of the requirement for excitation of the diene is that acyclic dienes, which do not absorb uv light filtered through Pyrex, are not subject to photoassistance.

Zeolite hole-catalyzed [2 + 2] dimerization of *trans*-anethole (**6**) has also been observed in a reaction which proceeds without photoassistance. Hole-catalyzed dimerization of **6** has previously been observed using the aminium salt catalyst and by photosensitized electron transfer and is especially facile because of the ease of ionization of this substrate (*12*). In contrast, β-methylstyrene, which lacks the electron-donating *p*-methoxy group, is only very inefficiently dimerized by zeolites, even with photoassistance. In both instances, competing Brønsted acid catalysis leads to formation of acyclic dimers.

Brønsted acid catalysis by zeolites is by no means new, but the smooth Brønsted acid catalysis of the dimerization of **8** is unprecedentedly efficient for a zeolite-catalyzed dimerization.

The principle of hole catalysis on heterogeneous surfaces, zeolites in particular, is an important one mechanistically and theoretically. Although the very limited scope and (at best) modest efficiency of the present zeolite catalyst systems obviously do not immediately qualify heterogenous hole-catalyzed pericyclic reaction procedures for broad synthetic or industrial use, it is hoped that the present results suggest the potential power of this catalytic principle and will encourage progress in the development of new and more effective catalyst systems.

ACKNOWLEDGMENTS

The research reported herein was supported by the Robert A. Welch Foundation (F-149) and by the National Science Foundation (CHE-8121700). The authors also thank Professor Paul Gassman for a private communication concerning the acid-catalyzed dimerization of **8**.

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Received November 5, 1984