Cross-Dehydrocycloaddition of 1,3-Butadiene with Isoprene over MgO and ZrO_2

Hiroyasu Suzuka and Hideshi Hattori*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received October 3, 1990)

A mixture comprising of equal amounts of 1,3-butadiene (BD) and isoprene (IPN) was allowed to react over MgO and ZrO_2 at 473 K in order to examine the relation between the product distribution and the reaction mechanisms. Over ZrO_2 the most abundant product was 4-ethyltoluene, which was produced by a base-catalyzed Diels–Alder reaction between BD and IPN, followed by double-bond migration and dehydrogenation. In the Diels–Alder reaction, IPN acts as a diene and BD acts as a dienophile. Over MgO, *o*-xylene was primarily produced by anionic mechanisms. Among the products formed from BD and IPN, 4-ethyltoluene was produced most, though the production of 3-ethyltoluene was considerable. The active sites on ZrO_2 were strongly poisoned by both CO_2 and NH_3. The active sites on MgO were completely poisoned by CO_2, and were modified by NH_3 in such a way that the reaction mechanisms changed from the anionic mechanisms to those involving the Diels–Alder reaction.

The dehydrocyclodimerization of dienes to aromatics has been reported to proceed over metal-acid bifunctional catalysts and solid acid catalysts at reaction temperatures above 673 K.[1–6] We recently found that the dehydrocyclodimerization of conjugated dienes to form aromatics proceeds over solid base catalysts even below 473 K. Among solid base catalysts, MgO and ZrO_2 exhibit high activity.[7] The product distribution over MgO is different from that over ZrO_2. In the dehydrocyclodimerization of 1,3-butadiene (BD), *o*- and *p*-xylenes were mainly produced over MgO, whereas ethylbenzene was the main product over ZrO_2. We proposed that different mechanisms operate in the reaction for MgO and ZrO_2.[8] Anionic intermediates are involved in the reaction over MgO, while the base-catalyzed Diels–Alder reaction precedes double-bond isomerization, followed by dehydrogenation over ZrO_2.

In the reaction of a mixture containing equal amounts of two different dienes, three different combinations of dienes result. In the case of a mixture containing equal amounts of BD and isoprene (IPN), products arising from combinations of BD–BD, BD–IPN, and IPN–IPN are possible. It is expected that the mechanistic differences are reflected in the product distribution caused by different combinations of the dienes. In the present study, a mixture of BD and IPN was allowed to react over MgO and ZrO_2 in order to examine how the differences in the mechanism reflect the product distribution in the cross-dehydrocycloaddition of BD with IPN.

Experimental

MgO was purchased from Merck. ZrO_2 was prepared from a 10% aqueous solution of $ZrOCl_2$ by hydrolysis with 28% aqueous ammonia to precipitate $Zr(OH)_4$ followed by washing with deionized water, drying at 373 K and calcining at 773 K.

The reactions were carried out in an all-glass H-shaped batch-type reactor. Two branches were separated by a breakable seal. A catalyst sample (200 mg) was placed in one branch, pretreated at 1073 K for MgO or 773 K for ZrO_2, and sealed. Since the product distributions were not significantly changed with the pretreatment temperature for both catalysts in the reaction of BD,[8] the pretreatment temperature was fixed at one temperature for each catalyst in the present study. The reactant, a mixture of 0.19 mmol BD and 0.19 mmol IPN, was stored in the other branch until it was introduced into the branch containing the catalyst thermostated at liquid-nitrogen temperature. The reaction was started by rapid melting of the reactant at the reaction temperature. Most of the reactions were run at 473 K for 17 h. The products were collected in a liquid-nitrogen trap and dissolved into 1 cm^3 of benzene, and then analyzed by gas chromatography. Styrene was used as an internal standard.

Poisoning experiments using carbon dioxide and ammonia as poisons were performed. Following a pretreatment of the catalyst, the poison was adsorbed at room temperature for 10 min, followed by evacuation at the same temperature for 10 min. The amounts of poisons adsorbed on the catalyst were measured as follows. The poisoned catalyst was heated to 1073 K, while the evolved poison was trapped in liquid nitrogen. The trapped poison was evaporated and measured volumetrically.

Results and Discussion

The product distributions in the reaction of a mixture containing equal amounts of BD and IPN, both with and without catalyst, are given in Table 1. Without catalyst, practically no reaction occurred at 393 K. At 473 K, though products resulting from the Diels-Alder reaction were formed, no aromatics were formed. The percentages of the products containing carbon numbers 8, 9, and 10 were 22, 52, and 26%, respectively. The ease to combine two diene molecules for a non-catalytic reaction is in the following order:

$$\mathrm{BD+IPN \gg IPN+IPN > BD+BD}$$

Table 1. Cross-Dehydrocycloaddition of 1,3-Butadiene and Isoprene

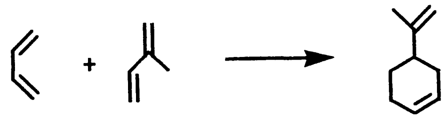
Catalyst	Reac. temp.	Yield of product[a)]/mol%										
	K	C_8	EB	*p*-X	*o*-X	C_9	4ET	3ET	CM	C_{10}	*m*-C	*p*-C
MgO	393	0.3	0	0	0	Trace	0	0	0	0	0	0
	473	0.6	1.6	2.3	4.8	0.4	1.2	0.9	0	0	0.7	0.3
ZrO_2	393	1.0	1.1	0	0	0.6	4.6	Trace	1.1	0	0	2.9
	473	Trace	4.8	0	0	0	6.9	1.8	2.6	0	0	2.4
None	393	Trace	0	0	0	0	0	0	0	0	0	0
	473	3.3	0	0	0	7.8	0	0	0	3.6	0	0

a) Mol of each product to 200 mol of a reactant mixture. C_8: dimer of 1,3-butadiene, EB: ethylbenzene, *o*-X: *o*-xylene, *p*-X: *p*-xylene, CM: isopropylbenzene (cumene), 4ET: 4-ethyltoluene, 3ET: 3-ethyltoluene, C_9: adduct of 1,3-butadiene to isoprene, C_{10}: dimer of isoprene, *p*-C: *p*-cymene, *m*-C: *m*-cymene. Gaseous compounds were produced, but not counted into calculation of composition. Catalyst weight 200 mg, Reactant: 1,3-butadiene 0.19 mmol, isoprene 0.19 mmol, Reaction time 17 h.

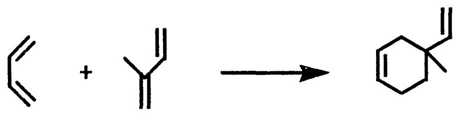
In the Diels-Alder reaction, both BD and IPN may act as a dienophile and diene. For the combination of BD with IPN, the possible reactions and the products are as follows:

1 (1)

2 (2)



3 (3)



4 (4)

In Eqs. 1 and 2, IPN acts as a diene and BD as a dienophile. In Eqs. 3 and 4, BD acts as a diene and IPN as a dienophile.

The product distributions among compounds containing carbon number 9, excluding aromatics, are given in Table 2. The relative amounts of 1-methyl-4-vinyl-1-cyclohexene (**1**): 1-methyl-5-vinyl-1-cyclohexene (**2**): 4-isopropenyl-1-cyclohexene (**3**): 4-methyl-4-vinyl-1-cyclohexene (**4**) were 8.5 (57.8%) : 1.3 (8.8%) : 3.6 (24.6%) : 1.3 (8.8%), which correspond to the reaction probability of equation (1) : (2) : (3) : (4). A reaction in which BD acts as a dienophile and IPN as a diene is predominant. This is expected because the Diels-Alder reaction is favored due to the presence of electron-releasing groups in the diene.

With a catalyst, the reaction proceeded to some extent, even at 393 K. In particular, the formation of

Table 2. Product Distribution of C_9 Products

Catalyst	Poison	Amount of poison	Reac. temp.	Product distribution/10^{-3} mmol			
		mol g^{-1}	K	1M4VCH[a)]	2M4VCH[b)]	4IPCH[c)]	4V4MCH[d)]
MgO	None		393	0	0	0	0
	None		473	0	0	0	0.7
	CO_2	2.3×10^{-4}	473	6.0	0.6	2.1	0.6
	NH_3	8.4×10^{-5}	473	0	0	0	0
ZrO_2	None		393	0	0	0	1.0
	None		473	0	0	0	0
	CO_2	2.7×10^{-4}	473	1.0	0	0	0
	NH_3	2.7×10^{-4}	473	4.2	0	1.9	0.6
None			393	0	0	0	0
			473	8.5	1.3	3.6	1.3

a) 1-Methyl-4-vinyl-1-cyclohexene. b) 1-Methyl-5-vinyl-1-cyclohexene. c) 4-Isopropenyl-1-cyclohexene. d) 4-Methyl-4-vinyl-1-cyclohexene.

aromatics was observed over ZrO_2 at this temperature. At 473 K, the product yields greatly exceeded those observed without a catalyst; the products consisted mostly of aromatics over both MgO and ZrO_2.

The product distributions were different for MgO and ZrO_2. Over ZrO_2, the percentages of the products containing carbon numbers 8, 9, and 10 were 26, 61, and 13, respectively. These percentages are close to those observed in non-catalytic product distribution, 22 : 52 : 26. The ease to combine two diene molecules for a ZrO_2-catalyzed reaction is in the following order:

$$\mathrm{BD}+\mathrm{IPN} \gg \mathrm{BD}+\mathrm{BD} > \mathrm{IPN}+\mathrm{IPN}$$

The combination of BD with IPN is the most favorable. A small difference in the combination between a ZrO_2-catalyzed reaction and a non-catalytic reaction is that the combination of two BD molecules is more favorable than that of two IPN molecules over ZrO_2. In a non-catalytic reaction, the combination of two IPN molecules is slightly favorable.

The relative amounts of C-9 aromatics produced over ZrO_2 were 4-ethyltoluene (6.9%), 3-ethyltoluene (1.8%), isopropylbenzene (2.6%). 4-Ethyltoluene, 3-ethyltoluene, and isopropylbenzene are formed from 1-methyl-4-vinyl-1-cyclohexene (**1**), 1-methyl-5-vinyl-1-cyclohexene (**2**) and 4-isopropenyl-1-cyclohexene (**3**), respectively, by successive double-bond migration and dehydrogenation. 4-Methyl-4-vinyl-1-cyclohexene (**4**) is not able to undergo double-bond migration and dehydrogenation and is difficult to convert to aromatics unless the C–C bond cleaves. The relative amounts of non-catalytic Diels–Alder reaction products are close to the relative amounts of the corresponding C-9 aromatics formed over ZrO_2, though the formation of 3-ethyltoluene over ZrO_2 was twice as great as that of 1-methyl-5-vinyl-1-cyclohexene by a non-catalytic Diels–Alder reaction.

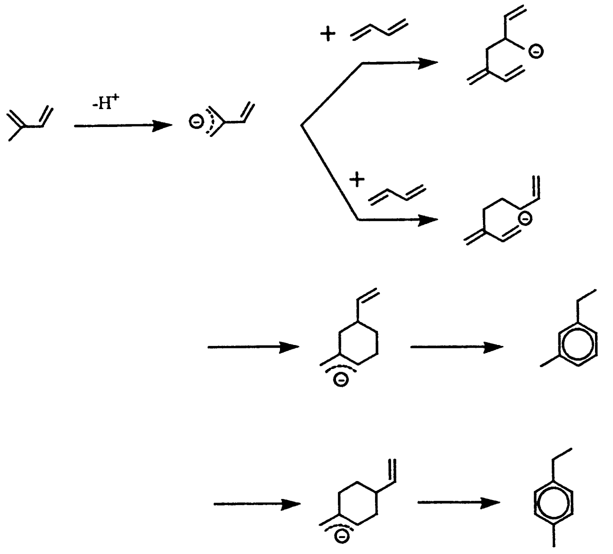
Almost the same percentages of the two main products over ZrO_2 (4-ethyltoluene and isopropylbenzene) to those produced without a catalyst (1-methyl-4-vinyl-1-cyclohexene and 4-isopropenyl-1-cyclohexene) suggest that dehydrocycloaddition results from a ZrO_2 catalyzed Diels–Alder reaction, followed by double-bond migration and dehydrogenation.

The percentages of the products for MgO were 73, 19, and 8% for products containing carbon numbers 8, 9, and 10, respectively, which are different from those for a non-catalytic reaction and a reaction over ZrO_2. The ease to combine two diene molecules over MgO is in the following order:

$$\mathrm{BD}+\mathrm{BD} \gg \mathrm{BD}+\mathrm{IPN} > \mathrm{IPN}+\mathrm{IPN}$$

A reaction involving two BD molecules is the most favorable combination over MgO. By this combination, *o*- and *p*-xylenes were mainly formed. As reported in a previous paper,[8] the formation of *o*- and *p*-xylenes results from anionic intermediates.

In the combination of BD with IPN, if an anionic mechanism is operating, 3-ethyltoluene would predominantly be formed as compared to 4-ethyltoluene, since the formation of 3-ethyltoluene involves a primary anion, while a less stable secondary anion is involved in the formation of 4-ethyltoluene, as illustrated below.



The ratio of 3-ethyltoluene to 4-ethyltoluene formed over MgO was 0.9/1.2, which is much larger than the ratio 1.8/6.8 over ZrO_2. This also supports the idea that the contribution of the anionic mechanism takes place to a considerable extent in a reaction over MgO, though the occurrence of a Diels–Alder reaction can not be neglected.

In the IPN molecule, the allylic hydrogen on the methyl group can be released much more easily as a proton. However, for the formation of isopropylbenzene by the anionic intermediate, an H atom on the carbon atom 4 of IPN should be abstracted, which is not plausible. Therefore, isopropylbenzene is difficult to form by an anionic mechanism. No isopropylbenzene was formed over MgO, in contrast to its formation over ZrO_2, which also suggests that the anionic mechanism is favored, compared with the Diels–Alder reaction over MgO.

As reported in the previous paper,[8] the active sites on ZrO_2 for dehydrocyclodimerization were completely poisoned by both carbon dioxide and ammonia. The poisoning effects on the active sites of MgO are different for carbon dioxide than for ammonia. Although carbon dioxide completely poisoned the active sites, ammonia modified them. The results of poisoning experiments for a mixture containing BD and IPN over MgO and ZrO_2 are given in Table 3. The amounts of the poisons retained on the surfaces were small compared with that of the reactant.

Although no aromatics were produced over the ZrO_2 poisoned by ammonia and carbon dioxide, the Diels–

Table 3. Cross-Dehydrocycloaddition of 1,3-Butadiene and Isoprene over Poisoned MgO and ZrO_2

Catalyst	Poison	Yield of product[a]/mol%										
		C_8	EB	*p*-X	*o*-X	C_9	4ET	3ET	CM	C_{10}	*m*-C	*p*-C
ZrO_2	None	Trace	4.8	0	0	0	6.9	1.8	2.6	0	0	2.4
	CO_2	1.4	0	0	0	0.6	0	0	0	0	0	0
	NH_3	2.2	0	0	0	3.6	0	0	0	1.3	0	0
MgO	None	0.6	1.6	2.3	4.8	0.4	1.2	0.9	0	0	0.7	0.3
	CO_2	2.1	0	0	0	4.9	0	0	0	2.3	0	0
	NH_3	0.4	0.7	0	0	0	1.0	0.4	0.3	0	0	0

a) Mol of each product to 200 mol of a reactant mixture. EB: ethylbenzene, *o*-X: *o*-xylene. C_8: dimer of 1,3-butadiene, *p*-X: *p*-xylene, CM: isopropylbenzene (cumene), 4ET: 4-ethyltoluene, 3ET: 3-ethyltoluene, C_9: adduct of 1,3-butadiene to isoprene, C_{10}: dimer of isoprene, *p*-C: *p*-cymene, *m*-C: *m*-cymene. Gaseous compounds were produced, but not counted into calculation of composition. Catalyst weight 200 mg, Reactant: 1,3-butadiene 0.19 mmol, isoprene 0.19 mmol, Reaction time 17 h, Reaction temperature: 473 K.

Alder reaction proceeded to some extent at the same level as those without a catalyst. The poisoning effect with ammonia on the activity of ZrO_2 was more severe than that with carbon dioxide. The product distribution was essentially the same as that for the non-catalytic type. The ZrO_2 poisoned by NH_3 was inert to the Diels-Alder reaction.

With a MgO catalyst, carbon dioxide completely poisoned all of the active sites. The product distribution was the same as that of the non-catalytic type.

Ammonia preadsorption decreased the activity of MgO to a small extent. However, marked effects by ammonia preadsorption appeared in the product distribution. Upon the adsorption of ammonia, the formations of *o*- and *p*-xylenes and 3-ethyltoluene greatly decreased, and isopropylbenzene, which was not formed on unpoisoned MgO, appeared. By an anionic mechanism, *o*- and *p*-xylenes as well as 3-ethyltoluene were favored; isopropylbenzene was unfavored. The decrease in the *o*- and *p*-xylenes and 3-ethyltoluene, and the formation of isopropylbenzene suggest that ammonia retards the formation of anionic intermediates, but not the Diels-Alder reaction and the following isomerization and dehydrogenation. This is consistent with the result of BD, as reported in a previous paper.[8] The relative ease to combine two diene molecules also changed upon ammonia preadsorption on MgO. The combination of BD with IPN became most favorable. The catalytic behavior of the MgO preadsorbing ammonia was similar to that of ZrO_2. Therefore, ammonia preadsorption modified the active sites on MgO so that the mechanisms for dehydrocycloaddition changed from one involving anionic intermediates to those involving a Diels-Alder reaction followed by isomerization and dehydrogenation.

References

1) T. K. Bhatia and M. J. Phillips, *J. Catal.*, **110**, 150 (1988).
2) S. M. Csicsery, *J. Catal.*, **17**, 207 (1970).
3) S. M. Csicsery, *J. Catal.*, **17**, 216 (1970).
4) S. M. Csicsery, *J. Catal.*, **17**, 315 (1970).
5) S. M. Csicsery, *J. Catal.*, **17**, 323 (1970).
6) S. M. Csicsery, *J. Catal.*, **18**, 30 (1970).
7) H. Suzuka and H. Hattori, *Appl. Catal.*, **47**, L7 (1989).
8) H. Suzuka and H. Hattori, *J. Mol. Catal.*, **63**, 371 (1990).