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Iodide Assisted Zeolite Catalysed 1,4-Addition of Water to Butadiene Monoxide

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Selective 1,4-addition of water to butadiene monoxide can be achieved in a liquid phase catalytic process using ultrastable Y zeolite as Brönsted acid, potassium iodide, and an ether solvent. The reaction mechanism could be elucidated based on the occurrence of intermediate reaction products. Iodide is added to the terminal unsaturated carbon atom of a protonated butadiene monoxide molecule. The strong solvent effect observed can be rationalised based on the nucleophilicity of the iodide depending on the basicity of the ether function. With USY zeolite, the 2-butene-1,4-diol selectivity reaches 73.9% at 100% conversion when using 1,2-dimethoxyethane solvent, 2,5-dihydrofuran being the main by-product. With this catalytic system followed by an additional hydrogenation step, butadiene monoxide can be selectively converted into 1,4-butanediol. © 1998 Academic Press

Key Words: **1,4-addition; butadiene monoxide; 2-butene-1,4-diol; ultrastable zeolite Y; potassium iodide.**

1. INTRODUCTION

1,4-Butanediol is an important chemical and intermediate, e.g. in the production of high performance polymers (1). For many years, the production of 1,4-butanediol has been based on the Reppe chemistry using acetylene (2). In the last two decades, there has been an increasing interest in the development of lower cost, large volume alternative processes for the manufacturing of 1,4-butanediol (3). Butane can be used as feedstock in a process involving oxidation into maleic anhydride and hydrogenation with or without esterification of maleic anhydride with ethanol (3, 4). The production of 1,4-butanediol can depart also from propylene oxide and proceed through formylation and hydrogenation steps (3, 5). One of the potential alternative feedstocks is 1,3-butadiene, a commodity petrochemical. One possibility for converting 1,3-butadiene into 1,4-butanediol involves oxidative diacetoxylation followed by hydrogenation and hydrolysis (5, 6). 1,3-Butadiene can be epoxidised into butadiene monoxide, e.g. over Ag/γ-alumina using dioxygen (6) or, alternatively, over titanium silicalite (TS-1) catalyst using hydrogen peroxide (7). The conversion of butadiene monoxide into 1,4-butanediol can be achieved by a four-step process comprising (i) a rearrangement of butadiene monoxide into 2,5-dihydrofuran, (ii) isomerisation into 2,3-dihydrofuran, (iii) ring opening, and (iv) hydrogenation (9).

In this paper we report an alternative two-step process for the conversion of butadiene monoxide into 1,4-butanediol, involving iodide assisted 1,4-addition of water to butadiene monoxide via heterogeneous catalysis on an acid zeolite.

2. METHODS

Butadiene monoxide (Aldrich, 98%), KI and organic solvents (Aldrich or Acros) were used as purchased. 37 wt% HI was from Merck. The USY zeolite was a CBV-720 sample with Si/Al ratio of 15 from PQ. It was dried at 373 K prior to use. Reactions were performed in a 100-ml stainless steel batch reactor-type 452 HC from PARR Instruments Corporation. In a typical reaction at 348 K, 0.7 g butadiene monoxide, 0.2 g USY, and 1.66 g KI, dissolved in a minimum quantity of distilled deionised water (7.2 g), were added to 20 ml 1,2-dimethoxyethane. USY can be replaced by 0.44 mmol of HI. In all experiments, the content of iodide in the reaction mixture was 10 mmol.

Analysis of the reaction products was performed by GC, while product identification was achieved with GC-MS.

3. RESULTS AND DISCUSSION

The use of HI in combination with a transition metal Lewis acid such as zinc iodide or tin iodide in an organic solvent was first reported in the rearrangement of butadiene monoxide into 2,5-dihydrofuran (10). Butadiene monoxide can be converted into 2-butene-1,4-diol in concentrated sulfuric acid in presence of KI with a selectivity of 69% at 95% conversion (11). In this work we investigated the use of an acid zeolite catalyst in combination with potassium iodide to achieve selective 1,4-addition.

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TABLE 1

Conversion (X_S) of Butadiene Monoxide after 3, 6, and 24 h of Reaction Time at 348 K Using Different Solvents and Acid Catalysts in the Presence of KI

Entry	Acid	Solvent	X_S (%) 3 h	6 h	24 h
1	HI	TME	79	96	99
2	USY	TME	23	61	92
3	HI	DME	7	26	95
4	USY	DME	81	97	100
5	HI	DIOX	6	18	98
6	USY	DIOX	7	11	53
7	HI	DEE	7	17	32
8	USY	DEE	6	10	50
9	HI	THF	17	33	88
10	USY	THF	3	4	39

Note. TME: 1,1,2-trimethoxyethane; DME: 1,2-dimethoxyethane; DIOX: 1,4-dioxane; DEE: diethylether; THF: tetrahydrofuran.

In agreement with literature (12), butadiene monoxide (**1**) was found to hydrolyse after 1 h at 373 K in water, mainly into 3-butene-1,2 diol (**2**). In organic solvents, butadiene monoxide is less reactive. In order to avoid solvolysis of butadiene monoxide, the solvents of choice were polar and aprotic. Alkanol solvents react with butadiene monoxide with formation of 1-hydroxy-2-alkoxy-3-butene (**3**), while the use of aldehydes and ketones results in a $(2+4)$ cycloaddition yielding, e.g. 2,2-dimethyl-4-allyl-1,3-dioxolane (**4**) with acetone as solvent. Butadiene monoxide showed excellent solubility in ether-type solvents.

Under the present reaction conditions and in the absence of KI, the hydrolysis of butadiene. monoxide resulted mainly in 3-butene-1,2-diol, whether the USY catalyst was added or not.

The butadiene monoxide conversion at 348 K in the presence of KI and HI or USY as acid catalysts and different ether solvents are reported in Table 1. High conversions can be reached with the homogeneous, as well as with the heterogeneous, acid catalyst, depending on the solvent used.

For the most active systems of Table 1, the selectivity after 24 h of reaction is reported in Table 2. With USY, the highest activity as well as 1,4-addition selectivity is found in 1,2-dimethoxyethane as solvent (Table 2, Entry 4). With HI as Brönsted acid, the highest 1,4-addition selectivity is obtained in 1,1,2-trimethoxyethane (Table 2, Entry 1). The highest selectivity for 2-butene-1,4-diol (**7**) product is obtained with USY as acid function (Table 2, Entry 4).

Based on the products obtained and their change in concentration with conversion, the reaction can be proposed (Fig. 1). 4-Iodo-2-butene-1-ol (**7**) was observed as the intermediate product. Consecutive nucleophilic substitution of iodide for hydroxide yields 2-butene-1,4-diol (**8**), while elimination results in the formation of 2,5-dihydrofuran (**9**). 1,2-Epoxide ring opening products containing iodide were not observed.

The positive ether solvent effect can be correlated with an enhancement of the nucleophilicity of iodide in these conditions. The strength of the dipole–dipole interaction between ether and KI, which controls the electron donation to potassium and thereby the nucleophilicity of iodide, is determined by the basicity of the ether linkage (13) (Fig. 2). This basicity is known to decrease in the following order:

$$\text{1,1,2-trimethoxyethane} > \text{1,2-dimethoxyethane}$$
$$\approx \text{1,4-dioxane} > \text{tetrahydrofuran} > \text{ethyl ether.}$$

TABLE 2

Effect of Type of Nucleophile and Acid on Activity and 1,4-Addition Selectivity in 1,2-Dimethoxyethane

Entry	Acid	Nucleophile	X (%) 3 h	X (%) 24 h	S (%)[a] 2-butene-1,4-diol	S (%)[a] 2,5-dihydrofuran	S (%)[a] 3-butene-1,2-diol	S (%)[a] Others	S (%)[a] 4-I-2-butene-1-ol	$S_{1,4}$[b] (%)
1	HI[c]	I^-	79.8	100	67.6	7.6	2.0	1.4[e]	20.7	96.1
2	USY[c]	I^-	24.8	93.8	61.9	7.5	7.3	3.0[e]	12.7	82.1
3	HI	I^-	9.5	99.5	52.2	28.4	10.8	0	7.6	88.2
4	USY	I^-	81.7	100	73.9	6.1	6.4	5.0[e]	8.4	88.4
11	HI	I^-+18-cr-6[d]	13.2	96.1	75.4	15.2	0	0	9.4	100
12	None	OH^-	0	10	0	0	70.9	29.1[f]	—	0
13	HI	Cl^-	77	99.3	7.3	0	66.8	25.9[g]	—	7.3
14	None	I^-	1.3	20.1	8.0	28.3	42.4	17.9[e]	3.4	47

[a] Selectivity after 24 h except for entry 1 and 4: after 6 h.

[b] Sum of the selectivities for 2-butene-1,4-diol, 2,5-dihydrofuran and 4-iodo-2-butene-1-ol.

[c] Solvent: 1,1,2-trimethoxyethane.

[d] 18-Crown-6 ether.

[e] Mainly 2-butenal (**6**) formed from 3-butenal (**5**) the thermally unstable rearrangement product of butadiene monoxide.

[f] Oligomers.

[g] 2-Chloro-3-butene-1-ol.

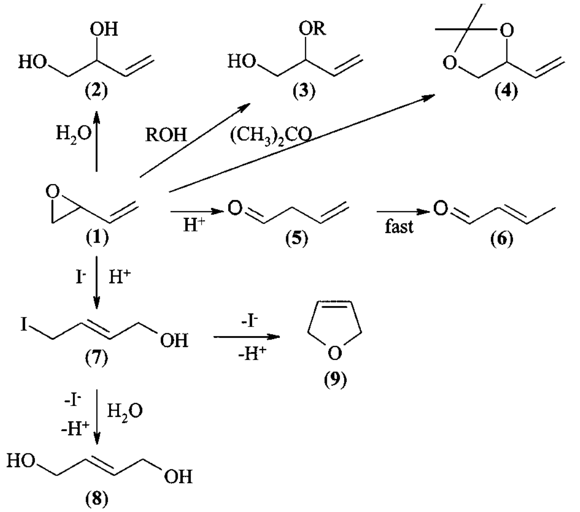

FIG. 1. Main and side reactions in the iodide assisted, acid catalysed hydrolysis of butadiene monoxide.

Cyclic ethers are better electron donors than acyclic ethers. Within the group of cyclic ethers, a decrease in the ring size results in less steric hindrance and a stronger complexation of dipolar compounds by smaller cyclic ethers (13).

Under homogeneous reaction conditions, the activity is higher in 1,1,2-trimethoxyethane compared with 1,2-dimethoxyethane and 1,4-dioxane, while the activity is lowest in ethyl ether. The high activity in tetrahydrofuran under homogeneous reaction conditions can be attributed to the presence of a sterically unhindered oxygen atom in the small ring structure. Both observations are in agreement with the proposed role of the solvent in the enhancement of the nucleophilicity of iodide. 18-Crown-6 ether is an even stronger potassium-complexing agent, compared with 1,1,2-trimethoxyethane. The addition of 5 mmol of 18-crown-6 ether enhances the activity and leads to the formation of 1,4-addition products only (Table 2, Entry 11).

The deviations from the expected solvent order in the presence of the USY zeolite can be explained by competitive sorption of solvent and substrate. 1,1,2-Trimethoxyethane has a higher molecular weight than butadiene monoxide, causing a decreased catalyst surface coverage of butadiene monoxide due to strong competitive adsorption of the solvent. A lighter ether, e.g. 1,2-dimethoxyethane, has an optimum molecular weight in this respect. The remarkably low reactivity of butadiene monoxide in cyclic ethers when using USY instead of homogeneous Brönsted acid (Table 1) points to the existence of steric constraints imposed on the solvated active complex by the zeolite cavities.

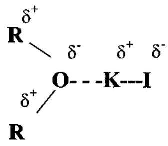

FIG. 2. Dipole–dipole interaction of KI with ether.

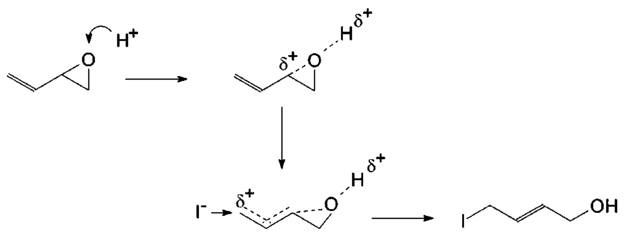

FIG. 3. Proposed stabilisation of the 1,4-transition state by the soft iodide nucleophile.

The high affinity of iodide for conjugate addition to butadiene monoxide can be attributed to its "soft base" character, which makes it most likely to react with a "soft acid," i.e. the activated butadiene monoxide with a charge, delocalised over the double bond (Fig. 3).

The hydroxide anion is a "hard base" and reacts with the "hard acid," i.e. the activated butadiene monoxide with localised charge. According to the HSAB principle, originally proposed by Pearson (14), it is known that halogenides can form π-bonds by donating electrons to the empty orbitals of the acceptor (15). In Table 2, Entry 12, the hydrolysis of butadiene monoxide was performed in 1,2-dimethoxy-ethane with NaOH addition. 1,4-Addition did not occur, as anticipated. The use of chloride, which has an intermediate hardness with respect to iodide and hydroxide, resulted in an intermediate selectivity for 1,4-addition (Table 2, Entry 13). In the absence of an acid catalyst and with potassium iodide, 1,4-addition dominates (Table 2, Entry 14). The latter reaction shows similarity to a Michael-type addition (16).

Under the reaction conditions of Table 1, Entry 4, USY catalysts samples with lower Al content (Si/Al = 30) or higher Al content (Si/Al = 2.7) were found to be less active and less selective for 2-butene-1,4-diol, compared to the USY sample with Si/Al = 15. The formation of by-products and especially 3-butene-1,2-diol and 2,5-dihydrofuran were enhanced.

The USY catalysts were found to deactivate in the catalytic experiments. They could be regenerated by washing with deionised, distilled water followed by drying at 373 K.

4. CONCLUSIONS

Butadiene monoxide can be converted selectively into 2-butene-1,4-diol and 2,5-dihydrofuran in a liquid phase catalytic process in ether solvents in the presence of KI and a Brönsted acid. USY zeolite is an appropriate heterogeneous acid catalyst. The presence of iodide is essential to obtain a high selectivity for 1,4 addition. The intermediate formation of 4-iodo-2-butene-1-ol suggests a reaction mechanism of iodide addition to the unsaturated terminal carbon atom, followed by substitution with hydroxide into 2-butene-1,4-diol or elimination and cyclisation into 2,5-dihydrofuran. With homogeneous Brönsted acid, the activity and selectivity are governed by the nucleophilicity of iodide, which can be enhanced by increasing the basicity of the ether solvent molecule. With the USY zeolite, the reactivities are altered by competitive adsorption of ether and butadiene monoxide molecules and sterical factors in the zeolite micropores. With the USY zeolite, the highest activity and 2-butene-1,4-diol selectivities were obtained in 1,2-dimethoxyethane solvent. With the new approach, butadiene monoxide can be converted into 1,4-butane diol in a two-step process, comprising the formation of 2-butene-1,4-diol followed by its hydrogenation.

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