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Transformation of 1,3-, 1,4- and 1,5-Diols over Perfluorinated Resinsulfonic Acids (Nafion-H)

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Abstract - The transformations of 1,3-, 1,4- and 1,5-diols over perfluorinated resinsulfonic acids (Nafion-H) were studied and correlations were examined between the structure of the investigated diols, the possible transformation directions and the catalytic properties of Nafion-H. Comparisons were also made between the catalytic properties of Nafion-H and zeolites. The characteristic transformations of 1,3-diols depend on their structure. 1,3-Propanediol undergoes dehydration via 1,2-elimination and yields oligomers via intermolecular dehydration. 1,3-Diols with an alkyl substituent on the carbon between those bearing the OH groups undergo 1,2-elimination yielding unsaturated alcohols and dienes, and give carbonyl compounds via the loss of water and hydride shifts analogous to the pinacol rearrangement. The strong acidity of Nafion-H and the lack of strong basic sites are advantageous for the latter reaction. 1,3-Diols with two substituents at this position mainly yield fragmentation products. Stereoselective cyclodehydration to the corresponding oxacycloalkanes is the characteristic transformation of 1,4- and 1,5-diols over Nafion-H.

INTRODUCTION

1,2-Diols as we reported recently¹ readily undergo dehydration over perfluorinated resinsulfonic acids, for instance, over Nafion-H catalyst. Nafion-H exhibits excellent activity under mild conditions relative to other solid electrophilic catalysts such as zeolites.² As it is well established for other electrophilic catalysts, the dehydration mainly proceeds via the pinacol rearrangement.^{3,4} The conditions (the relatively low temperature, 150-175 °C) and the strong acidity of Nafion-H comparable to that of concentrated sulfuric acid strongly favor the pinacol rearrangement versus 1,2-elimination.

In this paper we report the results of our investigations carried out with 1,3-, 1,4-, and 1,5-diols over Nafion-H catalyst. The catalytic features of Nafion-H and NaX zeolite are also compared.

In contrast with 1,2-diols, 1,3-diols lose water mainly via 1,2-elimination resulting in the formation of unsaturated alcohols and dienes as primary products under acid catalysis.³⁻⁵ Additionally, carbonyl compounds may also be formed via the loss of water and concomitant hydride shifts analogous to the pinacol rearrangement. The ratio of the two reactions (1,2-elimination and the formation of carbonyl compounds) depends on the structure of the diols. Diols without substituents on the carbon between those

bearing the OH groups, for example, 2,4-pentanediol, give products mainly through simple 1,2-eliminations. One alkyl substituent at this position increases the ratio of carbonyl compounds.⁶ When two alkyl substituents are present fragmentation is the dominant transformation.⁷ These main transformation directions of 1,3-diols are summarized in Fig. 1.

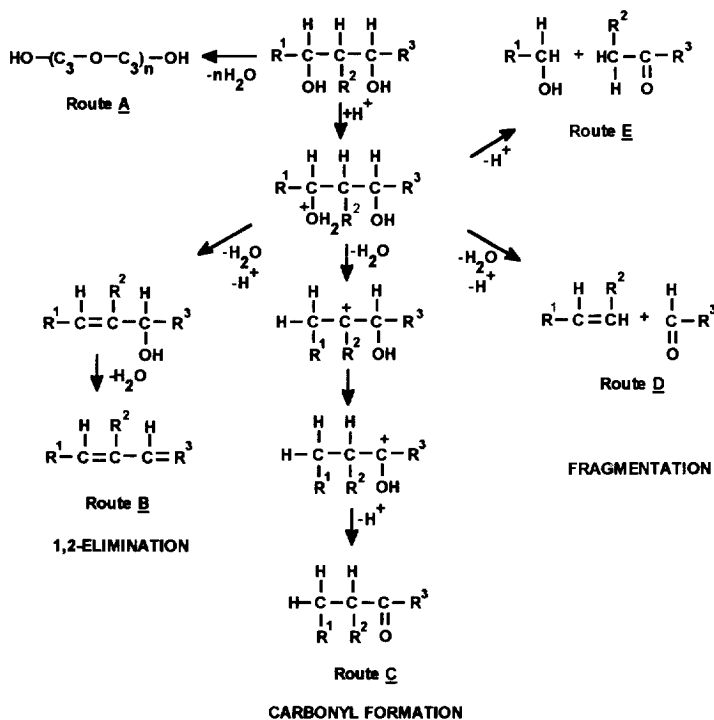


Fig. 1.

The characteristic transformation of 1,4- and 1,5-diols is cyclodehydration to yield the corresponding cyclic ethers (i.e., tetrahydrofuran and tetrahydropyran derivatives)^{3,4}, although 1,3-butadiene can also directly be synthesized from 1,4-butanediol under certain conditions. Olah and coworkers reported that Nafion-H is a superior catalyst for cyclodehydration.^{8,9}

RESULTS AND DISCUSSION

Transformation of 1,3-propanediol (1)

1,3-Propanediol (1) the simplest 1,3-diol gives a complex mixture of compounds formed via the possible primary and secondary transformation routes. Since oligomers or even polymers are present in this mixture, its accurate analysis is almost impossible. Primary products are formed via inter- and intramolecular dehydration. The intramolecular dehydration yields allyl alcohol via 1,2-elimination and propionaldehyde

via hydride shifts. Allyl alcohol undergoes secondary transformations (mainly hydrogen transfer reactions) to form 1-propanol. Some 2-propene-1-al (acrolein) can be also observed, although it readily reacts further via polymerization to resin-like materials under the conditions of our experiments. It should be mentioned that formation of 1,2-propadiene (allene) from allyl alcohol via a subsequent loss of water (the main reaction of 1,3-diols with longer carbon chain, *vide infra*) is not a thermodynamically favored transformation under these conditions.

Table 1. Ratio of the inter- and intramolecular dehydration of 1,3-propanediol (**1**) over Nafion-H and NaHX zeolite

	Intramolecular dehydration	Intermolecular dehydration	Conversion (%)
Nafion-H, 175 °C	16	84	49
NaHX, 275 °C	82	18	48

The data in Table 1 reveal that the intermolecular dehydration to oligomers of 1,3-propanediol (Fig. 1, route **A**) is the main transformation direction over Nafion-H at 175 °C. In contrast, intramolecular dehydration is the characteristic reaction over zeolites. The high selectivity of intermolecular dehydration over Nafion-H can be accounted for by the lower reaction temperature which, in general, favours intermolecular dehydration. It was found, for example, that primary and secondary alcohols transform via intermolecular dehydration to ethers at lower temperatures (ca. 100 °C) over Nafion-H catalyst, whereas at higher temperatures in the gas phase only alkenes are formed via intramolecular dehydration.¹⁰

Transformation of 1,3-butanediol (2)

Intramolecular 1,2-eliminations (Fig. 1, route **B**) are the main transformations of 1,3-butanediol (Table 2). The products are either unsaturated alcohols (NaX zeolite) or, by the loss of a second molecule of water, 1,3-butadiene (Nafion-H).

Table 2. Product distribution for 1,3-butanediol (**2**)

	Nafion-H	NaX
Products	175 °C	250°C
1,3-Butadiene	72	26
Unsaturated alcohols	17	64
Products of fragmentation	-	5
2-Butanone	4	3
Butanal	2	1
3-Buten-2-one	-	1
Unknown	5	-
Conversion (%)	38	33

Nafion-H favors the second dehydration step despite the lower temperature. In contrast with 1,3-propanediol intramolecular dehydration is the characteristic reaction accounted for by the presence of the secondary OH group which is more reactive in 1,2-elimination. Carbonyl compounds (2-butanone and butanal) are formed only in minor amounts.

Transformation of 2,4-pentanediol (3)

2,4-Pentanediol (3) a symmetrical disecundary diol was shown to have the ideal structure for diene formation through 1,2-eliminations over certain zeolites⁵. A similar conclusion can also be drawn in the case of Nafion-H, although the relative significance of the formation of carbonyl compounds increases substantially (Table 3). This change can be accounted for by the stronger acidity of Nafion-H as compared with that of zeolites. The lack of strong basic sites, however, should be also taken into account. The elimination of water through a bimolecular mechanism requires both an acidic and a relatively strong basic site the latter participating in the removal of a proton from an adjacent carbon atom. Nafion-H does not have any basic sites since the SO_3^- sites formed during the protonation of OH groups are very weak. The effect of the acid strength has been clearly demonstrated for faujasit type zeolites⁵. The higher the acid strength of the active sites, the more stable the intermediate oxonium ion-like transition state. A more stable transition state increases the possibility of hydride ion shifts resulting in a higher probability of the formation of carbonyl compounds vs. 1,2 elimination (increasing selectivity of 2-pentanone in the order $\text{NaX} < \text{NaY} < \text{NaHY}$).⁵

At low conversions acetal formation can take place resulting from the reaction of the starting diol and the primary product 2-pentanone yielding substituted stereoisomeric 1,3-dioxanes. Hence the total amount of the carbonyl compounds formed is the sum of the primary product carbonyl compound and the secondary product 1,3-dioxanes. With increasing temperature the ratio of the acetal formation decreases due to high diol conversion.

Table 3. Product distribution for 2,4-pentanediol (3)

Products	Nafion-H			NaX	NaHX
	125 °C	150 °C	175 °C	275 °C	275 °C
Pentadienes	55	48	70	90	53
Propene	-	-	-	-	2
Acetaldehyde	-	-	-	-	2
Acetone	-	-	-	2	7
Ethanol	-	-	-	-	4
2-Pentanone	2	5	8	2	1
Stereoisomeric 1,3-dioxanes	16	14	3	-	-
Unsaturated alcohols	27	32	19	6	2
3-Penten-2-on	-	-	-	-	29
Conversion (%)	3.5	59	89	90	98

Transformation of 3-methyl-2,4-pentanediol (4)

The methyl group on C(3) in 3-methyl-2,4-pentanediol (**4**) affects the relative ratio of the possible transformation routes shown in Fig. 1. First of all, a substantial further increase in the formation of carbonyl compounds vs. 1,2-elimination makes the former reaction the main transformation. Apparently, the methyl group at C(3) facilitates the thermodynamically strongly favored secondary to tertiary carbocation isomerization via a 1,2-hydride ion shift. A second 1,2-hydride shift and a proton loss results in the formation of the final product 3-methyl-2-pentanone. The observed selectivity changes also exclude a direct 1,3-shift from C(2) to C(4) as a possibility for the formation of carbonyl compounds. If the direct 1,3-shift were operative similar selectivities of carbonyl formation in the dehydration of **3** and **4** could be expected. It is worth mentioning, however, that 1,1-bis[hydroxymethyl]cycloalkanes (2,2-disubstituted-1,3-propanediols) particularly 1,1-bis[hydroxymethyl]cyclohexane under kinetic control do yield the corresponding carbonyl compounds via 1,3-hydride shift.¹¹

Table 4. Product distribution for 3-methyl-2,4-pentanediol (**4**)

Products	Nafion-H, 175 °C					NaX
	Converted diol fraction					275 °C
	1 ml	2 ml	3 ml	4 ml	5 ml	
Butenes	8	8	7	5	4	9
Acetaldehyde	4	3	3	2	2	11
Ethanol	1	0.5	0.5	0.5	0.5	7
2-Butanone	1	1	1	0.5	0.5	5
3-Me-pentadienes	16	19	26	33	38	47
3-Me-2-pentanone	48	47	43	40	38	15
2,4,5,6-tetraMe-1,3-dioxane	4	3.5	3	2	2	-
Unsaturated alcohols	12	12	11.5	10	9	3
Unknown	6	6	5	7	6	3
Conversion (%)	96.8	97.0	96.1	95.3	94.2	91.0

The methyl group at C(3), however, also facilitates fragmentation. Diols having two alkyl substituents on this carbon yield mainly fragmentation products either under homogeneous conditions (H_2SO_4)¹² or over faujasit type zeolites under heterogeneous conditions.⁷ We have made similar observations over Nafion-H. The fragmentation of diols can occur via two different routes. It may proceed through a carbenium ion or oxonium ion-like transition state via the well known β -scission (Fig. 1, route **D**) yielding an olefin and a carbonyl compound (2-butenes and acetaldehyde from 3-methyl-2,4-pentanediol). In addition, the protonated diol may undergo fragmentation via α -scission (Fig. 1, route **E**) to form a carbonyl compound and an alcohol (2-butanone and ethanol from 3-methyl-2,4-pentanediol). The probability of the two possible routes are almost identical in the fragmentation of **4** over faujasit type zeolites such as NaX (Table 4). In contrast, route **D** is the dominant transformation over Nafion-H which can be due

to the lower reaction temperature used. In addition, the stronger acidity of Nafion-H can also contribute to the change in selectivity since it results in a more efficient protonation of the OH groups facilitating β -scission.

As shown in Table 4 the ratio of the formation of carbonyl compounds to 1,2-elimination substantially decreases with the increasing amounts of diol converted, although the conversion decreases only slightly. In a deactivation process, in general, the most active sites can be presumed to be poisoned first. In our case, these are the active sites with the strongest acidity responsible for carbonyl formation. The parallel decrease of fragmentation also requiring strong acid sites is also in good accordance with this conclusion.

Transformation of 1,4- and 1,5-diols

It was found by Olah *et al.* that Nafion-H is a suitable catalyst for cyclodehydration of 1,4- and 1,5-diols to the corresponding cyclic ethers^{8,9}. Our experiments carried out with 1,4-butanediol (**5**) and 1,5-pentanediol (**6**) under continuous flow conditions gave results similar to those reported earlier. Both diols undergo dehydration yielding cyclic ethers with selectivities higher than 95% at conversions higher than 90%. The transformation of 2,5-hexanediol isomers (*d,l*-: **7a**, *meso*-: **7b**) provides an excellent possibility for the investigation of the stereochemical features of cyclodehydration. Data in Table 5 reveal that the cyclization is stereoselective. Secondary alcoholic OH groups are generally accepted to undergo dehydration by a bimolecular mechanism.¹³ As it is shown in Fig. 2 the backside attack of the OH group on the oxonium ion-like S_N2 transition state can be accounted for the selectivity.^{14,15}

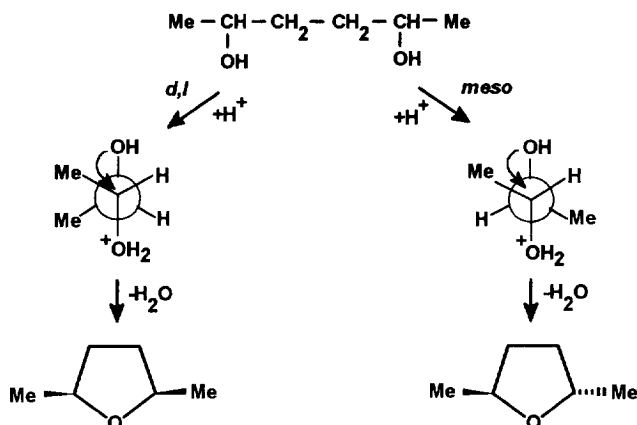


Figure 2.

Table 5. Product distribution for 2,5-hexanediol (8)

	2,5-Hexanediol (7)	<i>d,l</i> -2,5- Hexanediol (7a)	<i>meso</i> -2,5- Hexanediol (7b)
<i>cis</i> -2,5-diMe-tetrahydrofurane	46	94	3
<i>trans</i> -2,5-diMe-tetrahydrofurane	50	3	95
Unknown	4	3	2
Conversion (%)	91	93	92

CONCLUSIONS

Perfluorinated resinsulfonic acids, for instance, Nafion-H are suitable catalysts for the dehydration of 1,3-, 1,4-, and 1,5-diols. The characteristic transformation directions of 1,3-diols, similarly to other electrophilic catalysts, for example, zeolites⁵ depends on their structure. Diols unsubstituted at the carbon between those carrying the OH groups mainly undergo dehydration via 1,2-elimination to unsaturated alcohols and dienes. One alkyl substituent, for example, a methyl group at this position substantially increases the probability of the formation of carbonyl compounds via water loss and concomitant hydride shifts. The alkyl substituent facilitates the first hydride ion shift via a secondary to tertiary carbocation isomerization that is thermodynamically strongly favored. The strong acid sites of Nafion-H and the lack of strong basic sites make carbonyl formation even more favored. Fragmentation becomes the main transformation direction of 1,3-diols with two alkyl substituents. 1,3-Diols can undergo fragmentation via two different routes. The first one is the so-called β -scission widespread in the catalytic cracking processes. The second one is an α -scission resulting in an alcohol and a carbonyl compound. The relatively low temperature and the strong acidity of Nafion-H are advantageous for β -scission.

The characteristic transformation of 1,4- and 1,5-diols over Nafion-H is a stereoselective cyclodehydration to yield the corresponding oxacycloalkanes. The stereoselectivity is accounted for by an intramolecular S_N2 mechanism.

EXPERIMENTAL

Materials: 1,3-Propanediol, 1,3-butanediol, 2,4-pentanediol (1:1 isomeric mixture) 3-methyl-2,4-pentanediol, 2,5-hexanediol (1:1 isomeric mixture) and 1,5-pentanediol were Fluka products. They were purified by distillation before use. The isomers of 2,5-hexanediol were separated from the isomeric mixture via distillation of the isomeric oxepanes.¹⁵ Nafion-H was a DuPont product with an equivalent weight of 980 g/eq and an acid capacity of approximately 0.18 meq/g. NaX zeolite was purchased from Strem Chemicals. NaHX zeolite was prepared from NaX zeolite by Na^+ - NH_4^+ ion-exchange, followed by decomposition of the ammonium form at 400 °C for 5 h.¹⁶

Method: Experiments were carried out in a customary vertical fixed-bed reactor (length: 160 mm, inner diameter: 20 mm), which was electrically heated with a split-tube furnace. The temperature was controlled by a feedback controller. The reactor was charged with 1.5 g NAFION-H or with 1.5 g NaHX zeolite.

Fresh catalyst was used for each experiment. After pretreatment in dry nitrogen for 1 h (Nafion-H: at 150 °C, NaHX zeolite: at 400 °C) the catalysts were kept at the temperature of the experiment. NaHX zeolite gave an appropriate conversion only above 250 °C. Diols were introduced via a syringe pump at a weight hourly space velocity of 1 g/g.h. The liquid products emerging from the reactor were collected in a condenser cooled by cold water. The gaseous products were collected with a gas burette.

Analysis: Before GC and GC/MS analysis, the heterogeneous products (aqueous and organic layers) were homogenized by adding an appropriate amount of diglyme to the mixtures. The product distribution was determined with a Hewlett-Packard GC equipped with a 25 m PEG-20M capillary column and a flame ionization detector. The GC/MS investigations were performed on an HP-5890 GC instrument equipped with a 50 m HP-1 capillary column and an HP-5970 mass selective detector. Individual compounds were identified on the basis of their retention times (in comparison with authentic samples) or by using a MS library search method.

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