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Transformation of 1,2-Diols over Perfluorinated Resinsulfonic Acids (Nafion-H)

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Abstract - The transformations of 1,2-diols over perfluorinated resinsulfonic acids (Nafion-H) were studied, and correlations were examined between the structures of the investigated diols, the possible dehydration routes and the catalytic properties of Nafion-H. Comparisons were also made between the catalytic properties of Nafion-H and NaHX zeolite. Because of its stronger acidity, Nafion-H functions at temperatures considerably lower than those for the usual dehydrating catalysts, e.g. the zeolites. As is well established for other solid electrophilic catalysts, the dehydration of 1,2-diols mainly proceeds via the pinacol rearrangement. The lower temperatures and the stronger acidity of Nafion-H strongly favour the pinacol rearrangement versus 1,2-elimination. The reaction conditions are also advantageous for the formation of substituted 1,3-dioxolanes in a secondary condensation step between the unreacted diol and the primarily formed carbonyl compounds. Nafion-H gradually deactivates during long use, but it can be partially reactivated by washing with acetone.

INTRODUCTON

1,2-Diols transform readily on the action of electrophilic catalysts under either homogeneous (H_2SO_4, H_3PO_4, etc.) or heterogeneous (Al_2O_3, zeolites, etc.) conditions.[1-3] They undergo mainly dehydration to carbonyl compounds, unsaturated alcohols and dienes. Carbonyl compounds are formed via the pinacol rearrangement, through the 1,2-shift of a hydride anion or one substituent. Unsaturated alcohols and dienes are formed via 1,2-elimination. The ratio of the two dehydration transformations mainly depends on the structure of the diol, the acidic properties of the catalyst and the experimental conditions.[1,4] The pinacol rearrangement is usually the predominant transformation route. Besides dehydration, fragmentation also occurs, but usually to an extent of less than 5%.

Perfluorinated resinsulfonic acids (Nafion-H), with an acid strength comparable to that of concentrated sulfuric acid, are widely used as electrophilic catalysts in alkylation, acylation, isomerization, nitration, sulfonation, rearrangement, etc.[5-8]. Nafion-H is also able to catalyse the elimination of alcoholic OH groups. Aliphatic alcohols dehydrate to the corresponding ethers and alkenes, depending on the temperature and the structure of the carbon chain. For primary and secondary alcohols in the gas phase, it was found that low temperatures (ca. 100 °C) favoured ether production, while at higher temperature only alkenes were obtained.[9] On refluxing in benzene in the presence of Nafion-H, ditertiary 1,2-diols can be converted in excellent yield to the corresponding ketones, via the pinacol rearrangement.[10] In a previous investigation, 1,4-dioxane was the only identified product formed from 1,2-ethanediol over Nafion-H.[11]

Our work was initiated by the lack of systematic data on the transformation of 1,2-diols over Nafion-H. The aim of our investigation was to collect data by using diols with appropriate structures under different experimental conditions, to establish correlations between the structures of the diols, the reaction conditions and the possible transformation routes, and to compare the catalytic behaviour of Nafion-H and NaHX zeolite .

RESULTS AND DISCUSSION

Transformation of 1,2-ethanediol

The product distributions of 1,2-ethanediol (**1**) under the conditions of Method I and Method II at 175 °C are given in Table 1.

Table 1. Product distributions for1,2-ethanediol

	Nafion-H, 175 °C		NaHX
Products	Method I	Method II	250 °C
Acetaldehyde	6	2	38
Ethanol	-	-	11
2-Me-1,3-dioxolane	20	8	27
1,4-Dioxane	71	69	23
Diethylene glycol	-	13	-
Triethylene glycol	-	7	-
Unknown	3	1	1
	Reaction time: 19 h	Conversion: 55%	Conversion: 18%

Besides 1,4-dioxane, the only product identified previously[11], acetaldehyde is also formed from 1,2-ethanediol as a primary product of the pinacol rearrangement. The reaction conditions, i.e. the relatively low temperature as compared with that for NaHX zeolite, favours formation of 2-methyl-1,3-dioxolane as a secondary product via a subsequent condensation step between acetaldehyde and 1,2-ethanediol. Under continuous flow circumstances, linear oligomers of 1,2-ethanediol (mainly diethylene glycol and triethylene glycol) can also be separated and identified. Intermolecular dehydration too takes place under the distillation conditions, but the compounds formed can not distill out of the reaction flask because of their high boiling points, and they therefore cleave back to the starting compound. The difference between the product distributions for Nafion-H and NaHX zeolite can be explained by the different reaction temperatures. NaHX zeolite is not able to dehydrate 1,2-ethanediol at 175 °C, the temperature of the experiments with Nafion-H. Because of the entropy factor, the higher temperature (250 °C) does not favour intermolecular dehydration to 1,4-dioxane or linear oligomers. Similarly, condensation to 2-methyl-1,3-dioxolane is not favored either. In fact, decomposition of the substituted 1,3-dioxolanes can be observed under similar conditions.

Transformation of 1,2-propanediol

In contrast with 1,2-ethanediol (**1**), 1,2-propanediol (**2**) is transformed mainly via the pinacol rearrangement exclusively to propionaldehyde (Table 2).

Table 2. Product distributions for 1,2-propanediol (**2**)

	Nafion-H, 175 °C		NaHX
Products	Method I	Method II	250 °C
Propionaldehyde	13	74	61
Acetone	<1	5	18
trans-2-Et-4-Me-1,3-dioxolane	48	11	-
cis-2-Et-4-Me-1,3-dioxolane	32	8	-
2,2,4-triMe-1,3-dioxolane	4	2	-
1-Propanol	-	-	7
Allyl alcohol	-	-	10
Unknown	2	-	4
	Reaction time: 3.5h	Conversion: 82%	Conversion: 76%

The yield of acetone, the other possible product of the pinacol rearrangement, is strikingly low (5%). In contrast, 12-30% acetone is formed over zeolites though at a higher temperature (250 °C)[4] (18% over NaHX zeolite). The higher acidity of Nafion-H and the lower temperature further favour elimination of the secondary OH group to give propionaldehyde. Theoretically, the formation of propionaldehyde is conceivable through the isomerization of allyl alcohol formed as a primary product via 1,2-elimination. Nevertheless, allyl alcohol itself does not undergo any change under similar conditions. The considerably shorter reaction time (3.5 h) as compared with that for the diprimary 1,2-ethanediol (19 h) is due to the higher dehydration ability of the secondary OH group.

Transformation of 2,3-butanediol

The transformations of the 2,3-butanediol isomers provide an excellent possibility for investigation of the stereochemical features of the pinacol rearrangement. The experimental data on the mixture of 2,3-butanediol isomers (**3**) and the pure *meso-* (**3a**) and *d,l-* (**3b**) isomers are given in Tables 3 and 4.

As shown in Table 3, transformation of the mixture of 2,3-butanediol (**3**) isomers yields a very complex mixture of primary products formed via the pinacol rearrangement and via 1,2-elimination, and of the secondary products of acetal formation between the starting diol and the carbonyl compounds. Identification of the possible 2-ethyl-2,4,5-trimethyl-1,3-dioxolane and 4,5-dimethyl-2-propyl-1,3-dioxolane isomers was not successful, even when the GC/MS library search method was used. Accordingly, their sum is given in the Tables.

Table 3. Product distributions for 2,3-butanediols (**3**)

	Nafion-H				NaHX
	Method II			Method I	
Products	125 °C	150 °C	175°C	175 °C	250 °C
1-Butene	1	1	2	-	2
1,3-Butadiene	2	4	8	3	16
2-Me-propanal	-	1	4	1	4
2-Butanone	41	63	80	14	78
2-Et-2,4,5-triMe-1,3-dioxolane isomers	43	24	4	67	-
4,5-diMe-2nPr-1,3-dioxolane isomers	13	7	2	15	-
Conversion (%)	36	87	100	1.5 h*	59

*reaction time

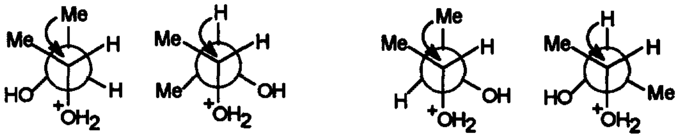
As in general, 2,3-butanediol (**3**) is transformed mainly via the pinacol rearrangement to give 2-butanone as primary product. Under appropriate conditions, in the distillation method and in the continuous flow experiments at low conversion, the corresponding 1,3-dioxolane derivatives are also formed. This transformation becomes the main reaction route at 125 °C. The rate of 1,2-elimination, the possible transformation concurrent with the pinacol rearrangement, resulting in the formation of 1-buten-2-ol and 1,3-butadiene, is considerably lower than with zeolites.[4] A possible explanation, supported by the data in Table 3, can be given in terms of the entropy factor. This favours 1,2-elimination and its effect increases with increasing temperature. The higher strength of the acid sites of Nafion-H should also be taken into consideration. The higher the acid strength of the active sites, the more stable the intermediate oxonium ion-like transition state. A more stable transition state favours the shift of a hydride ion or methyl anion, resulting the pinacol rearrangement. The effect of the acidic strength has been clearly demonstrated for NaX and NaHX zeolites.[4]

The diastereoisomeric 2,3-butanediols differ in two ways (Table 4). First, the *d,l*-isomer possesses higher reactivity. Second, the *meso*-isomer yields more 2-methylpropanal via the pinacol rearrangement. Similar observations were made with Al_2O_3 as catalyst under heterogeneous conditions[12] and with phosphoric acid as catalyst under homogeneous conditions.[13] These differences can be explained by the steric hindrance existing between the substituents in the transition state of the pinacol rearrangement. Secondary alcoholic OH groups are generally accepted to undergo dehydration by a bimolecular mechanism.[14] It has been clearly demonstrated for the dehydration of diols over zeolites that the bimolecular mechanism operates for both the pinacol rearrangement and 1,2-elimination.[4,15]

Table 4. Product distributions for *meso-* and *d,l*-2,3-butanediol under the conditions of Method II

	meso-2,3-Butanediol (3a)			*d,l*-2,3-Butanediol (3b)		
	Nafion-H		NaHX	Nafion-H		NaHX
Products	150 °C	175 °C	250 °C	150 °C	175 °C	250 °C
1-Butene	<1	2	<1	<1	2	<1
1,3-Butadiene	1	8	17	1	6	13
2-Me-propanal	<1	3	7	<1	1	1
2-Butanone	70	83	76	60	87	86
2-Et-2,4,5-triMe-1,3-dioxolane isomers	18	3	-	35	3	-
4,5-diMe-2-nPr-1,3-dioxolane isomers	10	1	-	3	1	-
Conversion (%)	78	97	76	91	99	96

Analysis of the possible four E2 transition states for dehydration of the 2,3-butanediol isomers (Fig. 1) reveals that three of them (**a**, **b** and **c**) involve a significant gauche interaction of the methyl groups. The lack of the gauche interaction in the transition state **d** (Fig. 1) may explain both the mentioned observations. The higher stability of transition state **d** causes the higher reactivity of the *d,l*-isomer. Further, the preferred formation of 2-butanone from the *d,l*-isomer can also be accounted for by the favoured shift of the hydride ion in transition state **d**.



a **b** **c** **d**

meso-2,3-butanediol (3a) *d,l*-2,3-butanediol (3b)

Fig. 1.
E2 transition states of *meso*-(**3a**) and *d,l*-2,3-butanediol (**3b**)

The effect of the reaction conditions on the aldehyde/ketone ratio too must be taken into consideration. Ordinarily, lower temperature and weaker acids favour aldehyde formation, for the aldehydes themselves are irreversibly converted to ketones under more drastic conditions.[16] In fact, the ratio of 2-methylpropanal decreases with increasing temperatures, and NaHX zeolite (with weaker acidic strength) gives more aldehyde than Nafion-H even at higher temperature.

As in general[17], cyclic acetal and ketal formation is also stereoselective under the circumstances of these experiments.

Transformation of 2,3-dimethyl-2,3-butanediol

The transformation of 2,3-dimethyl-2,3-butanediol (**4**) (pinacol), the parent compound in the pinacol rearrangement, results in a very similar product distribution (Table 5) to that for zeolites at higher temperatures.

Table 5. Product distributions for pinacol (**4**)

Products	Nafion-H	NaHX
	Method I, 175 °C	250 °C
2,3-diMe-1,3-butadiene	21	24
3,3-diMe-2-butanone	75	74
Unknown	4	2
	Reaction time: 0.6 h	Conversion: 92%

The increase in the extent of 1,2-elimination as compared with 2,3-butanediol (**3**) can be explained by the different mechanism operating in the case of pinacol (**4**). Pinacol dehydrates via a monomolecular mechanism due to its tertiary OH groups. Formation of a carbon-carbon double bond by the elimination of a proton from the adjacent carbon atom is more favourable for the free carbenium ion transition state of the E1 mechanism than for the E2 transition state.

Catalytic Properties of Nafion-H

Nafion-H also possesses good catalytic properties in the dehydration of 1,2-diols under either continuous flow or distillative conditions. Because of its higher acidity, it functions at considerably lower temperatures than zeolite dehydrating catalysts. The higher acidity of Nafion-H and the lower reaction temperature favour the pinacol rearrangement versus 1,2-elimination. The reaction conditions are also advantageous for condensation of the starting diols and the primarily formed carbonyl compounds to yield substituted 1,3-dioxolanes.

No exact turnover numbres could be determined because of the complexity of the possible primary and secondary transformations.

The data from longer term experiments (Table 6) reveal that the activity of Nafion-H decreases only slightly with increasing amount of diol converted, and the originally white Nafion-H becomes dark-brown or black. A similar colour change is observed when Nafion-H is heated in air at 175 °C. During the transformation of 25 ml diol on 1.5 g catalyst the conversion decreases from 100% to 84 % over a period of 25 hours. The partially deactivated resin can be reactivated by washing with acetone five times, though the original activity can not be fully restored (Table 6).

The data demonstrate that the product distribution changes continuously during the deactivation. With decreasing conversion, the amount of 1,3-dioxolane derivatives formed from unreacted diol and the primarily formed carbonyl compounds increases. After reactivation, the product distribution is quite similar to that obtained during transformation of the 10th ml of diol.

Table 6. Product distributions in long term experiment on 2,3-butanediol (**3**)

	Converted diol fraction					
Products	1ml	5ml	10ml	15ml	25ml	reactivated
Butenes	1	2	2	2	2	1
1,3-Butadiene	8	5	3	1	1	3
2-Me-propanal	5	3	2	1	1	2
2-Butanone	83	82	82	79	66	83
1,3-Dioxolane derivatives	3	8	11	17	30	11
Conversion (%)	100	99	97	94	84	96

CONCLUSIONS

1,2-Diols can be dehydrated with perfluorinated resinsulfonic acids (Nafion-H) under relatively mild conditions as compared with other electrophilic solid catalysts, e.g. zeolites. The characteristic transformation route, as in general, is the pinacol rearrangement. The higher acidity of Nafion-H and the lower reaction temperature make the pinacol rearrangement even more favoured. The reaction conditions are also especially advantageous for the formation of cyclic acetals and ketals from the unreacted diol and the carbonyl compounds formed during the primary dehydration step.

The product distributions reveal that the dehydration of diols takes place by a bimolecular mechanism in the case of secondary OH groups, and it is very likely that diols containing tertiary OH groups undergo transformtion by a monomolecular mechanism, with formation of a free carbenium ion in the first stage.

EXPERIMENTAL

Materials

1,2-Ethanediol (**1**), 1,2-propanediol (**2**), a mixture of 2,3-butanediol isomers (**3**) and 2,3-dimethyl-2,3-butanediol (**4**) (pinacol) were FLUKA products. The mixture of 2,3-butanediol isomers was separated into the *meso*-(**3a**) and *d,l*-isomers (**3b**) by fractional distillation of the corresponding cyclic ketals formed with acetone.

Nafion-H was a DuPont product with an equivalent weight of 980 g/eq and an acid capacity of approximately 0.18 meq/g. NaHX zeolite was prepared from NaX zeolite (Strem Chemicals) by Na^+-NH_4^+ ion-exchange, followed by decomposition of the ammonium form at 400 °C for 5 h.[18]

Apparatus and experiments

Method I (distillation) - A 25 ml round reaction flask containing 0.1 mole diol and 1 g Nafion-H catalyst was equipped with a Claisen distilling head. The reaction mixture was heated at 175 °C. Products distilled off as they are formed.The quantity of gaseous products was measured with a gas burette.

Method II (continuous flow) - 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 (Nafion-H: at 150 °C, NaHX zeolite: at 400 °C in dry nitrogen for 1 h), the reactor was 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 measured as mentioned above.

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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