J. Chem. Research (S), 1999, 326–327†

Cyclodehydration of Some 1,*n*-Diols Catalysed by Sulfated Zirconia†

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Sulfated zirconia, a solid acid, is found to be a good catalyst in the cyclodehydration of several diols.

Cyclodehydration of diols is a useful method to obtain oxygen heterocycles. In particular, the cyclodehydration of butane-1,4-diol to tetrahydrofuran (THF) and of diethylene glycol (DEG) to 1,4-dioxane are industrially important reactions. Such reactions of diols are effected in the liquid or gas phase using mineral and organic acids,[1] calcium phosphate,[2] HMPT,[3] clay,[4] alumina,[5] PPh_3-CCl_4,[6] Nafion,[7] *etc.* We have earlier reported the efficacy of group IV metal halides and metallocenes[8] and of H-ZSM5[9] in such cyclodehydration reactions.

Herein, we report our results on the use of sulfated zirconia (SO_4^{2-}/ZrO_2) in such reactions. The catalytic features of H-ZSM5 and SO_4^{2-}/ZrO_2 are also compared. As is evident from Table 1 butane-1,4-diol and pentane-1,5-diol furnish the respective cyclic ethers, *e.g.* tetrahydrofuran and tetrahydropyran in respectable conversion and high selectivity. However, hexane-1,6-diol yields a mixture of oxepine, tetrahydro-2-methyl-2*H*-pyran, 4-methyl-1-penten-3-ol, hexenols and dienes in the proportion of 43:15:23:16:3. Cyclohexane-1,4-diol also reacts similarly to give a mixture of products that include oxabicyclo[2.2.1]heptane and cyclohexadienes. Both diethylene glycol (DEG) and triethylene glycol (TEG) react to give 1,4-dioxane. TEG furnishes 1,4-dioxane in 73.5% selectivity at 47% diol conversion. The conversion of TEG to 1,4-dioxane may involve the scission of TEG to 1,4-dioxane and ethylene glycol (EG) and EG thus formed would react with another molecule of TEG to give higher oligomers.[9]

Table 1 Cyclodehydration of diols over SO_4^{2-}/ZrO_2 (catalyst : diol = 1 : 25 w/w)

Entry	Substrate	*t*/min	*T*/°C	Conv.[a] (%)	Selectivity[b]	Yield[c] (%)	Product(s)
1	Butane-1,4-diol	60	130	74	96	0.22	THF
2	Pentane-1,5-diol	85	155	93	94	0.24	THP
3	Hexane-1,6-diol	60	175	55			Mixture[d]
4	DEG (first cycle)	120	180	83	89.5	0.19	1,4-Dioxane
	(av. three cycles)	270	180	85	84.5	0.5	1,4-Dioxane
5	Cyclohexane-1,4-diol	60	145	79			Mixture[e]
6	TEG	85	180	47	73.5	0.08	1,4-Dioxane

[a] Conversion of diol = (total diol − unreacted diol/total diol) × 100. [b] Selectivity of product = (moles of product obtained/moles of diol converted) × 100. [c] Yield of product = (moles of product formed/weight of catalyst in g). [d] Oxepine, 2-methyl-2*H*-pyran, 4-methylpent-1-en-3-ol, hexenols, hexadienes. [e] Oxabicyclo[2.2.1]heptane, cyclohexadienes.

The reusability of this catalyst was examined for the cyclodehydration of DEG with fresh DEG added to the reaction flask after completion of the first cycle. Three cycles were carried out at 180 °C (Table 1). The DEG conversion and 1,4-dioxane selectivity after the first cycle were 83 and 89.5% while for the three cycles on average, values were 85 and 84.5%, respectively. At 200 °C (Table 3) the yield of 1,4-dioxane was higher than that obtained at 180 °C.

Some properties of the catalysts are given in Table 2.[10] It was of interest, to compare the catalytic features of SO_4^{2-}/ZrO_2 with those of H-ZSM5[9] as both exhibit acidic character. Accordingly, DEG was subjected to cyclodehydration over SO_4^{2-}/ZrO_2 at 200 °C similarly to H-ZSM-5 (Table 3). While SO_4^{2-}/ZrO_2 could be easily recycled six times, cyclodehydration over H-ZSM-5 did not extend beyond the second cycle after 4 h. The results as evident from Table 3 suggest that SO_4^{2-}/ZrO_2 is more effective in the selective cyclodehydration of DEG to 1,4-dioxane. The relative efficiency of some catalyst systems in the cyclodehydration of DEG to 1,4-dioxane is shown in Table 4 which includes results with Nafion-H. The cyclodehydration of diols involves the Brönsted acid sites of the catalyst.[9] For hexane-1,6-diol and cyclohexane-1,4-diol, 1,2-elimination appears to be responsible for the formation of unsaturated alcohols and olefins in the product mixtures. This alludes to the interaction of both the OH groups of the diol with the catalyst surface in the cyclodehydration mechanism. Interestingly, when hexan-1-ol and cyclohexanol were similarly reacted over SO_4^{2-}/ZrO_2, the former did not react even at 150 °C whereas the latter was dehydrated to give a moderate amount of cyclohexene. This shows that secondary hydroxy group facilitates 1,2-elimination in cyclohexanol and

Table 2 Properties of catalysts

Catalyst	Surface area/ $m^2\,g^{-1}$	Pore volume/ $cm^3\,g^{-1}$	Density/ $g\,cm^{-3}$	Acidity[a]/ $mol\,g^{-1}$
SO_4^{2-}/ZrO_2	16.8	8.76	1.24	9.48×10^{-4}
H-ZSM5	310		0.8	3.9×10^{-4}

[a] Determined by NH_3 adsorption method. [b] Si/Al = 40.

Table 3 Cyclodehydration of DEG over H-ZSM5 and SO_4^{2-}/ZrO_2 at 200 °C

	H-ZSM5	SO_4^{2-}/ZrO_2
No of cycles	1	6
Total run time/h	4	4
Total DEG conversion	63	86
1,4-Dioxane selectivity	67	85
Yield of 1,4-dioxane (mole/g of catalyst)	0.16	0.82

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† IPCL Communication No. 337. This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 4 Cyclodehydration of DEG over catalyst systems

Catalyst	t/h	T/°C	Yield of 1,4-dioxane, (mole/g of catalyst)
SO_4^{2-}/ZrO_2	2	180	0.19
H-ZSM5	4	200	0.16
Al^{3+}-montmorillonite K10[4]	3	200	0.16
Nafion-H	4	175	0.025
HMPT[3]	17	220	0.010
Al_2O_3[5]	21	220–250	0.005

cyclohexanediol.

From this study it is clear that SO_4^{2-}/ZrO_2 is a useful catalyst in the cyclodehydration reaction of diols.

Experimental

All the chemicals used were of reagent grade and obtained from Aldrich, USA; E. Merck, Germany and Glaxo, India. SO_4^{2-}/ZrO_2 was prepared according to the literature method.[10] Reaction products were analysed on Shimadzu 7AG and 15A GC columns using 1.5% OV-17 and 15% Carbowax 20M coated on shimalite and a flame ionization detector. GC–MS investigations were performed on an HP 5890 GC instrument equipped with HP 5970 mass selective detector. Individual compounds were identified on the basis of their retention time (in comparison with authentic samples) or by using the MS library search method. The acidity of the catalysts and other physical properties were measured by standard methods.[10]

Typical Procedure.—Butane-1,4-diol (8.00 g) and SO_4^{2-}/ZrO_2 (300 mg, H_0 between −3.0 and −5.6) were heated at 130 °C in a microdistillation set up and THF and water distilled out. The reaction was stopped after 60 min as the distillation slowed down significantly. Both the distillate and reactant were quantitatively analysed by GC using a suitable internal standard.

We thank IPCL management for permission to publish this work and Mr A. B. Parikh for technical assistance.

Received, 15th September 1998; Accepted, 28th January 1999
Paper E/8/07189F

References

1 M. Bartok and A. Molnar, *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogues*, ed. S. Patai, John Wiley, New York, 1980, p. 721.

2 H. Huchler, S. Winderl, H. Mueller and H. Itoffman, *Ger. Pat.*, 2 503 750, 1976 (*Chem. Abstr.*, 1976, **85**, 142983).

3 J. Diab, M. Abov-Assali, C. Gervais and D. Anker, *Tetrahedron Lett.*, 1985, **26**, 1501.

4 D. Kotkar and P. K. Ghosh, *J. Chem. Soc., Chem. Commun.*, 1986, 650.

5 Y. Inoue, S. Deguchi and T. Hakushi, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3031.

6 C. N. Barry and S. A. Evans Jr., *J. Org. Chem.*, 1981, **46**, 3361.

7 I. Basci, A. Molnar, M. Bartok and G. A. Olah, *Tetrahedron*, 1995, **53**, 3319.

8 A. Wali, P. A. Ganeshpure, S. M. Pillai and S. Satish, *Ind. Eng. Chem. Res.*, 1994, **33**, 444.

9 A. Wali, S. M. Pillai, S. Unnikrishnan and S. Satish, *J. Mol. Catal. A*, 1996, **109**, 149.

10 A. Wali, S. Unnikrishnan, S. M. Pillai and S. Satish, *Indian J. Chem. Technol.*, 1998, **5**, 172.