JOURNAL OF CATALYSIS 72, 322–327 (1981)

Studies on the Conversions of Diols and Cyclic Ethers

I. Investigation of Part-Steps in the Dehydration and Fragmentation of 1,3-Diols on a Copper Catalyst

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Received April 16, 1981; revised August 3, 1981

Reaction rate measurements were used to study the two characteristic transformations of 1,3-diols on a Cu/Kieselguhr (Cu/k) catalyst: dehydration to an oxo compound containing the same number of carbon atoms, and dealdolization with formation of two molecules of oxo compound. The model compounds were 1,3-butanediol, which undergoes the former transformation, and 2-methyl-2,4-pentanediol, which undergoes the latter. It was found that the intermediate β-hydroxy-oxo compounds may be formed by hydrogen transfer or by catalytic dehydrogenation. These react further by dehydration or by dealdolization. The data were used to interpret the connection between the transformation directions and the molecular structure. It was concluded that the copper catalyst participates in the individual part-processes, but the dealdolization and the dehydration, in which α,β-unsaturated oxo compounds are formed, may also take place thermally. The data also allowed an interpretation of the difference between the copper-catalyzed transformations of 1,2- and 1,3-diols: the reactivities of the 1,2- and 1,3-diols were explained on the basis of the different rates of transformation of the α- or β-hydroxy-oxo compounds formed from them.

INTRODUCTION

The inter- and intramolecular dehydration of organic compounds containing hydroxy groups on the action of oxide catalysts is a well-known process that has been studied widely and in detail. Substantially fewer data are known on dehydration in the presence of metals, since metals are primarily used as dehydrogenation–hydrogenation catalysts. Studies in this field have been carried out mainly by Pines and coworkers (*1*), particularly as regards the dehydrating activity of nickel, leading to the formation of ethers. The elimination of water from diols on the action of metals is similarly a process that is rarely investigated. The knowledge relating to transformations leading to the formation of oxo compounds or cyclic ethers, depending on the structure, has been reviewed (*2*).

This special property of the metals is mainly of theoretical significance, for the study of these processes may also contribute to the interpretation of the mechanism of action of metal catalysts. This is supported by the fact that metal-catalyzed dehydration is now being dealt with in greater detail, particularly recently (*1*, *3*–*8*). The necessity of further examinations is justified in that it has not yet been clearly demonstrated what the role of the metal is in these dehydrations (*1*, *4*, *5*).

As one of the first results of our comprehensive investigations connected with the metal-catalyzed reactions of the diols, we discovered a new transformation of 1,3-diols (a reaction characteristic of 1,2-diols under different reaction conditions): dehydration with the formation of oxo compounds (*9*). It subsequently appeared logical to carry out a detailed investigation on this group of compounds, in the course of which we studied the stereochemistry (*10*) and mechanism (*11*) of the dehydration of 1,3-diols on various copper catalysts. It was established that, depending on the structure, two main processes occur: dehy-

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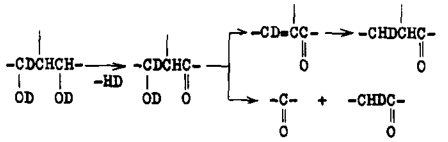


SCHEME 1

dration to an oxo compound with the same number of carbon atoms, and fragmentation to two molecules of oxo compounds. With deuterium-labeled compounds the reaction scheme shown in Scheme 1 was confirmed; among others, it was demonstrated that the transformations proceed via a common intermediate, a β-hydroxy-oxo compound.

In our most recent investigations we have performed reaction rate measurements to characterize the above transformation directions further. The chosen model compounds were 1,3-butanediol, which is converted to an oxo compound containing the same number of carbon atoms, and 2-methyl-2,4-pentanediol, the main reaction of which is fragmentation.

EXPERIMENTAL

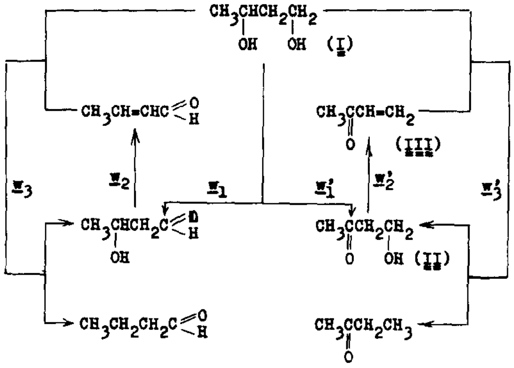
Measurements were made as described previously (*11*), in a flow reactor on a Cu/k catalyst with a grain size of 0.25–0.4 mm (the k support is Merck Kieselguhr) (*12*). For every measurement, fresh catalyst (0.1 g) was taken; this was activated for 75 min at 150°C in a hydrogen stream of 5 ml · min^{-1} and for 75 min at 200°C in a hydrogen stream of 15 ml · min^{-1}, and then maintained at the temperature of the measurement for 30 min (heating-up period 15 min). The temperature was regulated to an accuracy of ±0.1°C with a PID (proportional-differential-integral) regulator.

TABLE 1

Some Characteristic Data on the Kieselguhr and the Cu/k

	Cu/k	Kieselguhr
BET surface area (m^2 g$_{\text{catal.}}^{-1}$)	27.00	1.00
Acidic centers (meq g$_{\text{catal.}}^{-1}$)	0.20	0.02
Basic centers (meq g$_{\text{catal.}}^{-1}$)	1.01–0.31[a]	0

[a] Depending on the time of reduction.

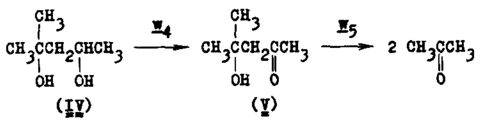


SCHEME 2

The surface areas of the catalyst and the support were determined with the BET method, and the number of active centers by titrimetry (*13*) (Table 1).

The 1,3-butanediol (I) was a commercially available product (BDH), while the 4-hydroxy-2-butanone (II), 2-methyl-2,4-pentanediol (IV), 4-methyl-4-hydroxy-2-pentanone (V), and 3-hydroxy-2-butanone (VI) were synthesized on the basis of known literature methods. Their GC purities were 100% (based on standard compounds).

In the course of the measurements, the correlation was determined between the conversion and the mass velocity (Table 2) (the conversion was measured by means of GC, with the aid of calibration curves). The reaction rates *w* were obtained from the data by graphical differentiation, and then from the resulting data by extrapolation to infinite mass velocity (Table 3).



SCHEME 3

TABLE 2

Experimental Results

Compound	Reaction	Temp. (°C)	B^a	S^b	Conversion (mol%)	
					Primary OH	Secondary OH
I	Formation of hydroxy-oxo compound (Scheme 2)	220	12.0	3.72	9.5	27
			11.5	3.56	9.5	28.5
			5.4	1.67	16	41
			5.1	1.58	17	42
			3.8	1.18	20	48
II	Catalytic dehydration (Scheme 2)	220	10.5	3.39	29	
			5.8	1.87	41	
			4.1	1.32	49	
			3.9	1.26	50	
		190	5.8	1.87	31	
			5.6	1.81	32	
			3.1	0.98	46	
			3.0	0.97	47	
			2.1	0.68	51	
	Thermal dehydration	190	5.7	0.73	18	
			3.3	0.43	25	
			2.3	0.30	30	
			2.2	0.28	30	
			1.9	0.24	33	
	Dealdolization (Scheme 4)	220	10.5	3.39	3	
			5.8	1.87	4.5	
			4.1	1.32	5	
			3.9	1.26	5	
IV	Dehydrogenation (Scheme 3)	210	6.4	1.39	17	
			5.4	1.18	20	
			4.5	0.98	22	
			3.9	0.85	23	
			3.4	0.74	25	
			3.2	0.70	26	
V	Catalytic dealdolization (Scheme 3)	173	21.8	4.89	23	
			12.0	2.69	35	
			5.5	1.23	53	
			3.6	0.81	77	
	Thermal dealdolization	173	6.9	1.55	5	
			4.2	0.94	7	
			2.2	0.49	11	
			1.1	0.25	19	
VI	Dehydration (Scheme 5)	270	6.0	1.91	16	
			5.6	1.78	16	
			2.2	0.70	23.5	
			2.0	0.64	24	

[a] B: feed rate (ml h^{-1}).

[b] S: mass velocity (mol $g_{catal.}^{-1}$ $s^{-1} \times 10^{-4}$).

TABLE 3

Reaction Rates Calculated from the Experimental Data

	Catalyst	Temp. (°C)	Reaction rate (mol $g_{catal.}^{-1}$ $s^{-1} \times 10^{-3}$)
Hydrogen transfer (Scheme 2)	Cu/k	220	$w_1 + w_3 = 5.3$
Hydrogen transfer (Scheme 2)	Cu/k	220	$w_1' + w_3' = 18.3$
Dehydration (Scheme 2)	Cu/k	220	$w_2' = 15.0$
Dehydration (Scheme 2)	Cu/k	190	$w_2' = 8.2$
Thermal dehydration (Scheme 2)	k	190	$w'_{2,\text{ therm}} = 1.8$
Dealdolization (Scheme 4)	Cu/k	220	$w_2'' = 1.6$
Dehydrogenation (Scheme 3)	Cu/k	210	$w_4 = 4.2$
Dealdolization (Scheme 3)	Cu/k	173	$w_5 = 15.8$
Thermal dealdolization (Scheme 3)	k	173	$w_{5,\text{ therm}} = 0.1$
Dehydration (Scheme 5)	Cu/k	270	$w_6 = 4.5$

RESULTS AND DISCUSSION

Formation of β-Hydroxy-oxo Compounds

The data in Table 3 indicate that the β-hydroxy-oxo compounds are formed by two different mechanisms in the cases of **I** and **IV**. In our earlier studies on **I** (*11*), it was established that the dehydration leading to the oxo compound is a three-step process involving two intermediates (Scheme 1). However, the dehydrogenation step and the hydrogenation of the unsaturated oxo compound must occur in one step, by hydrogen transfer (Scheme 2).

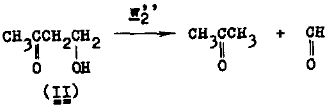
In the dehydrogenation of **IV**, there is no possibility for such a hydrogen transfer, and thus the formation of **V** from this compound proceeds via a simple catalytic dehydrogenation. The two discrete mechanisms may be supported by a comparison of the results of the rate measurements: the rate of formation of **II** ($w_1' + w_3' = 18.3$) is much higher than that for the dehydrogenation of **IV** ($w_4 = 4.2$), in spite of the fact that in both cases a secondary hydroxy group undergoes transformation.

Transformation of the Hydroxy-oxo Compounds

For the different 1,3-diols, the two main transformation directions outlined in Scheme 1 generally proceed in parallel, to various extents. Their proportions are governed by the structure of the intermediate β-hydroxy-oxo compound: the dealdolization leading to the formation of the two oxo compounds is characteristic of the more highly substituted compounds. For the two compounds examined in the present work, the transformations occur as main reactions: **II** primarily undergoes dehydration, and **V** dealdolization (Schemes 2 and 3).

A comparison of the rates of transformation of **II** and **V** (w_2' and w_5), with consideration of the value found for the slight dealdolization of **II** (w_2'', Table 3, Scheme 4), shows that the dealdolization accelerates to a greater degree as the substitution increases, and accordingly this becomes the main reaction in the case of **V**.

A comparison of the data obtained on the support alone with those found on the copper catalyst ($w'_{2,\text{ therm}}$ and w_2'; $w_{5,\text{ therm}}$ and w_5, respectively) gives a clear-cut answer to the question of whether certain centers on the catalyst play a role in the transformations. The fact that both processes undergo an acceleration on the copper catalyst can be explained by the increase in the surface area, i.e., both can take place as a thermal



$$\underset{\substack{\Vert \\ O}}{CH_3C}CH_2\underset{\substack{| \\ OH}}{CH_2}\ \xrightarrow{w_2''}\ CH_3\underset{\substack{\Vert \\ O}}{C}CH_3 + \underset{\substack{\Vert \\ O}}{CH_2}$$

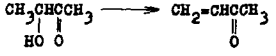
(II)

SCHEME 4

reaction too. (It is well known that certain β-hydroxy-oxo compounds are readily dehydrated, while thermal dealdolization occurs with other compounds (*14–16*); at the same time, acids and bases are also good catalysts of both processes (*17, 18*).) However, the ratios of the rates measured for the two processes ($w'_2/w'_{2,\,\mathrm{therm}} \approx 5$; $w_5/w_{5,\,\mathrm{therm}} \approx 150$) demonstrate that the thermal process too may play a role in the dehydration, while the dealdolization mainly takes place on the action of the various catalyst centers.

Reactivities of 1,2- and 1,3-Diols

Our investigations indicated the characteristic transformation of 1,2-diols on various copper catalysts, primarily at comparatively low temperature (200–240°C), is dehydrogenation yielding the α-hydroxy-oxo compounds, i.e., these compounds are not converted to the oxo compounds, or only with great difficulty (ditertiary 1,2-diols are exceptions) (*19*). The dehydrations of **VI**, as an α-hydroxy-oxo compound, and **II**, as a β-hydroxy-oxo compound, lead to the same product, methyl vinyl ketone (**III**). A comparison of the rates of these dehydrations (w_6 and w'_2; Schemes 5 and 2) clearly reveals the cause of this phenomenon: the transformation of **VI** is several orders of magnitude slower. Thus, the intermediate formed by dehydrogenation from the 1,2-diol cannot undergo further transformation under the given experimental conditions for molecular structural reasons; this is in contrast with the β-hydroxy-oxo compounds formed from the 1,3-diols, which readily yield oxo compounds by rapid elimination of water or by dealdolization.



$$CH_3\underset{HO}{\underset{|}{CH}}\underset{O}{\underset{\|}{C}}CH_3 \xrightarrow{w_6} CH_2{=}CH\underset{O}{\underset{\|}{C}}CH_3$$

(VI) (III)

SCHEME 5

CONCLUSIONS

Our investigations show that, depending on the molecular structure, the transformations of the 1,3-diols to β-hydroxy-oxo compounds may occur by hydrogen transfer or by dehydrogenation, these processes being catalyzed by copper. Hydrogen transfer takes place when the intermediate β-hydroxy-oxo compound undergoes dehydration, for the α,β-unsaturated oxo compound then formed is able to participate in such a process. The multiply substituted β-hydroxy-oxo compounds are transformed by dealdolization, in a fast reaction. Both the dehydration and the dealdolization may also occur as thermal processes, but it has been clearly demonstrated that the active centers of the supported copper catalyst are of determining importance in the transformations.

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