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Dehydration Mechanism of Gaseous 2-Butanol-2-d_1 over Salt Catalysts

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Dehydration can either proceed as a two-step mechanism (E1 or E1cB) or as a one-step mechanism (E2). In the dehydration of 2-butanol-2-d_1 according to a two-step mechanism, a loss of deuterium in all butenes would be observed; in a concerted mechanism the original content of deuterium would be retained.

The dehydration of 2-butanol-2-d_1 and 2-butanol-d_0 was studied over $Ca_3(PO_4)_2$, BPO_4, $Ba_3(PO_4)_2$, $CaHPO_4$, and $AlPO_4$ in the range of temperature between 150 and 460°C using microcatalytic and mass spectrometric techniques. The catalytic reactivity of deuterated and undeuterated butanols is equal. From the loss of deuterium in the butenes, a minimum value of the percentage of the two-step mechanism is estimated. The visible maximum value is obtained from the yield of 2-butene in the dehydration of 1-butanol.

The loss of deuterium of 2-butanol-2-d_1 (caused by two-step mechanisms) is taken into account for correcting former results. Eighty-eight and eighty-one percent syn E2 were found over $Ca_3(PO_4)_2$ at 300 and 400°C, respectively. After correction, 89% syn E2 were obtained at 300°C and 88% at 400°C. This shows the temperature dependence of the percentage of the E1 mechanism.

INTRODUCTION

Dehydration can proceed according to a one-step (E2) or a two-step (E1 or E1cB) mechanism. In the dehydration of 2-butanol-2-d_1 according to a pure E2 mechanism, only deuterated butenes should be formed. A loss of deuterium in the butenes can be considered as indicative of a two-step mechanism being involved. In this way a determination of the percentage of the mechanisms is possible.

In earlier studies (*1–5*) the percentage of two-step mechanisms was determined using 1-butanol. In addition, the isomerization of butenes was measured. In the case of a pure E2 mechanism, only 1-butene is formed from 1-butanol: formation of 2-butenes shows the existence of an E1 mechanism. Now, 1-butanol reacts less readily than 2-butanol, the difference in the reaction temperature being about 100°C. However, the percentage of E1 mechanism decreases with falling temperature (*1*). The percentage values of E1 mechanism obtained from 1-butanol therefore represent the visible maximum values, and it is difficult to relate these values to the temperatures at which 2-butanol reacts.

For the purposes of the present paper it is appropriate to be able to refer directly to some of the data obtained in previous studies (*4*). Table 1 summarizes relevant results on the 2-butene yield from 1-butanol and isomerization of butenes. Assuming a pure stereoselective E2 elimination from threo-2-butanol-3-d_1 (97% D) and erythro-2-butanol-3-d_1 (100% D), the syn E2 or anti E2 preference was calculated in an

TABLE 1

2-Butene Yield from 1-Butanol and Isomerization of Butenes

Catalyst	2-Butene yield		Isomerization	
	°C	%[a]	°C	%[b]
$Ca_3(PO_4)_2$	340	8	340	7
	400	35	400	30
BPO_4	150	No conversion	150	20
	260	74	260	70
$Ba_3(PO_4)_2$	400	15	400	Below 1
$CaHPO_4$	350	10	350	3
$AlPO_4$	320	11	320	Below 1

[a] The difference to 100% is the 1-butene yield.

[b] 1-Butene and *cis*-2-butene were pulsed separately. With each reactant nearly the same degree of isomerization (production of the other butenes) was found. The average values are listed, indicated as sum of the butenes formed (all butenes, i.e., reactants and products, = 100%).

earlier paper (*4*). In a concerted mechanism, the 1-butene should retain the original content of deuterium. Two-step mechanisms lead to a loss of deuterium in the butenes which can only be recognized in 1-butene. Data concerning a loss of deuterium in 1-butene and the calculated mechanisms, which were found in preceding studies, are given in Table 2.

EXPERIMENTAL

Microcatalytic (*8*) and mass-spectrometric techniques were used. The quantities pulsed were 0.5 µl (for the alcohols) or 0.5 ml (for butenes), the amount of catalyst being 100 mg and the flow rate 25 ml of He/min. The column was 13.5% bis-(2-methoxyethyl)-adipate and 6.5% diethylsebacinate on chromosorb R 60–80 mesh, diameter $\frac{1}{8}$ in.; the length was 6 m and the temperature was 25°C. Retention times were: air, 1 min 30 s; 1-butene, 7 min 20 s; *trans*-2-butene, 9 min; and *cis*-2-butene, 10 min 10 s. A mass-spectrometer (GC/MS Varian MAT 111) served as detector for the deuterated substances.

The catalysts were $Ca_3(PO_4)_2$, $CaHPO_4$, and $Ba_3(PO_4)_2$ (Baker-Chemicals); $AlPO_4$ (Riedel-de Haën); BPO_4 (EGA-Chemie). The catalysts were dried for several days at 150°C. Before starting the dehydration, the catalysts were treated at the lowest temperature of reaction for 2–3 hr in a flow of helium.

The reactants were 2-butanol-2-d_1 (deuterium content: 99% D) (Roth) and 2-butanol puriss (Fluka).

RESULTS

Table 3 gives a comparison between the catalysts in the dehydration of 2-butanol-2-d_1 and 2-butanol-d_0. Each value is the average of at least three measurements.

The values of the distribution of products of 2-butanol-2-d_1 and 2-butanol-d_0 are practically equal. Hence, there is no isotope effect.

For all the catalysts (except BPO_4) the loss of deuterium in the temperature range

TABLE 2

Threo- and erythro-2-Butanol-3-d_1: Percentage of Deuterated Molecules of 1-Butene and Calculated E2 Mechanisms

Catalyst	Temperature of dehydration (°C)	Substances	1-Butene (%D)	syn/anti-E2 ratio
$Ca_3(PO_4)_2$	275–320	erythro	100	86/14
320[a]		threo	98	87/13
	375	erythro	98	82/18
		threo	95	81/19
$CaHPO_4$	305–340	erythro	100	67/33
360[a]		threo	97	71/29
$Ba_3(PO_4)_2$	330–400	erythro	100	67/33
450[a]		threo	97	72/28
	460	erythro	99	72/28
		threo	96	72/28
$AlPO_4$	265–300	erythro	100	43/57
300[a]		threo	97	47/53
	400	erythro	97	49/51
		threo	92	51/49
BPO_4	145	erythro	85	59/51
200[a]		threo	90	51/49
	165	erythro	81	49/51
		threo	92	53/47
	200	erythro	80	49/51
		threo	89	52/48
	300	erythro	39	49/51
		threo	43	49/51

[a] Temperature of 100% conversion (°C).

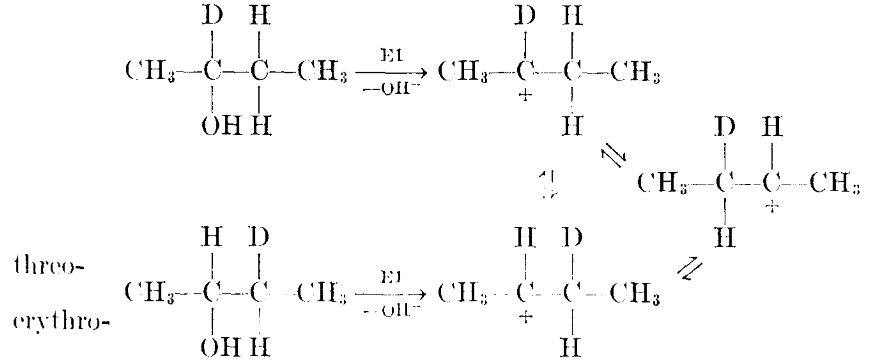
of 100% conversion is slight and practically constant. Only at higher temperatures is a decrease of deuterium observed. However, with BPO_4 the loss of deuterium is much higher at all temperatures. At temperatures below 100% conversion, it is practically constant for *trans*-2-butene and *cis*-2-butene.

DISCUSSION

The dehydration of 2-butanol-2-d_1 according to the E1 mechanism produces a secondary carbonium ion in the first step, which can be converted into another carbonium ion (see scheme of reactions below) and (or) into the corresponding butenes by splitting off H^+ or D^+. A loss of deuterium can easily be explained by a two-step mechanism. A two-step mechanism, however, can also leave the content of deuterium unchanged.

The loss of deuterium in the butenes indicates the minimum value of the two-step mechanisms. The visible maximum value is obtained in the dehydration of 1-butanol from the sum of the produced 2-butenes.

A comparison of Tables 2 and 3 shows that the loss of deuterium of threo-(erythro-)2-butanol-3-d_1 and 2-butanol-2-d_1 in 1-butene is rather similar. On the one hand, this fact can be explained by the equal catalytic reactivity. On the other hand, the same intermediate stage can be formed in the dehydration of the reactants mentioned before.



Seifert and Noller (*7*) found a similar result. They studied the isomerization of 1-butene with $MgSO_4$ as catalyst and DCl as co-catalyst. They found equal distribution of deuterium between C_1 and C_2 in monodeuterated 2-butene and interpreted this by a "hydrogen bridge mechanism."

Correction of the Former Calculation of Mechanisms

In a former paper, the mechanistic calculations concerning the E2 mechanisms were based upon the assumption that the percentage of E1 mechanism is zero. This is a simplification, as one can see from Tables 1 and 2. The present study gives us the possibility to make a more precise estimation of the percentage of the mechanisms.

A rigorous calculation of the percentage of E1 is difficult. But it is possible to estimate an upper and lower limit of E1. The deuterium loss found in 1-butene is similar with the reactants 2-butanol-2-d_1 and erythro(threo)-2-butanol-3-d_1. It is low and increases somewhat with temperature (see Tables 2 and 3). It is a reasonable assumption that in an E1 mechanism the deuterium loss observed in 2-butenes should also be similar for all the above reactants. This is actually found with BPO_4, a catalyst with a high E1 percentage (*4*). Of course, in E2 mechanisms the content of deuterium of the

TABLE 3

Product Distribution with 2-Butanol-2-d_1 (A) and 2-Butanol (B) (Sum of 1-Butene, *trans*-2-Butene, and *cis*-2-Butene = 100%) and Percentage of Deuterated Molecules of Each Species (in Parentheses)

Catalyst	Temperature (°C)	Reactant	1-Butene	*trans*-2-Butene	*cis*-2-Butene
$Ca_3(PO_4)_2$	280–320[a]	A	26 (97)	33 (97)	41 (96)
		B	27	33	40
	350[b]	A	28 (97)	33 (96)	39 (95)
		B	29	33	38
	400[b]	A	26 (94)	36 (92)	38 (84)
		B	26	36	38
	460[b]	A	28 (75)	37 (73)	35 (63)
		B	26	39	35
BPO_4	165	A	10 (84)	38 (70)	52 (68)
	160	B	8	39	53
	180	A	11 (80)	39 (71)	50 (68)
		B	10	39	51
	195	A	12 (76)	39 (70)	49 (68)
	200	B	12	40	48
	250[c]	A	16 (62)	43 (52)	41 (52)
		B	15	45	40
	300[c]	A	18 (45)	45 (40)	37 (40)
		B	18	44	38
$Ba_3(PO_4)_2$	350–425[a]	A	32 (97)	26 (96)	42 (97)
		B	31	25	44
	465[d]	A	34 (95)	26 (95)	40 (95)
		B	35	27	38
$CaHPO_4$[e]	300–360[a,f]	A	29 (98)	26 (97)	45 (96)
	300–340[a]	B	31	26	43
$AlPO_4$	270–300[a]	A	22 (97)	37 (93)	41 (94)
		B	23	39	38
	400[g]	A	26 (96)	36 (92)	38 (90)
		B	27	36	37

[a] The percentage of deuterated molecules and the product distribution were practically equal in this temperature range.

[b] Conversion 100% [of A and B at $Ca_3(PO_4)_2$] at 320°C.

[c] Conversion 100% at 200°C.

[d] Conversion 100% at 450°C.

[e] Above 350°C decomposition of catalyst and formation of diphosphates (*6*).

[f] Conversion 100% at 360°C.

[g] Conversion 100% at 300°C.

2-butenes must depend upon the reactant so that the loss of deuterium caused by two-step mechanisms cannot be observed. Since the 2-butenes obtained from 2-butanol-2-d_1 should not lose deuterium in a pure E2 mechanism, the observed deuterium loss of 2-butenes was used for estimating the percentage of E1 (see Table 4).

The loss of deuterium in 2-butanol-2-d_1 amounts to 2% in 1-butene, 1% in *trans*-2-butene, and 4% in *cis*-2-butene at a temperature of 300°C. These percentages are added to the corresponding contents of deuterium in the butenes obtained from threo-2-butanol-3-d_1.

At 300°C the following corrected values

TABLE 4

Product Distribution with threo-2-Butanol-3-d_1 and 2-Butanol-2-d_1 (sum of 1-Butene, *trans*-2- and *cis*-2-Butene = 100%), Percentage of Deuterated Molecules of Each Species (in Parenthesis) and Calculated E2 Mechanism (without Corrected Two-Step Mechanisms) over $Ca_3(PO_4)_2$

Temperature (°C)	Reactant	1-Butene	*trans*-2-Butene	*cis*-2-Butene	syn/anti E2 ratio
300	threo	34 (98)	26 (19)	40 (93)	88/12
	2-butanol-2-d_1	27 (97)	32 (98)	41 (95)	
400[a]	threo	35 (95)	27 (24)	38 (85)	81/19
	2-butanol-2-d_1	26 (94)	36 (92)	38 (84)	

[a] Conversion 100% at 320°C.

are found: 34% 1-butene (100% D), 26% *trans*-2-butene (19, 2% D), and 40% *cis*-2-butene (96, 8% D). In the same way the mechanism was calculated and the result was 89/11 syn/anti ratio of the E2 mechanism.

At 400°C 81% syn E2 mechanism was found for the reaction of threo-2-butanol-3-d_1. After taking into account the loss of deuterium (1-butene 5%, *trans*-2-butene 7%, and *cis*-2-butene 15%), 88% syn E2 was found. This difference was a result of the percentage of two-step mechanisms which increased with temperature and affected the calculation of the syn E2 mechanisms. In the same way over the other catalysts the E2 mechanisms were calculated (Table 5).

TABLE 5

Corrected and Previously Calculated (in Parenthesis) Percentage of syn E2 Mechanism Obtained from threo- and erythro-2-Butanol-3-d_1

Catalyst	Temperature (°C)	syn E2 mechanism (%)	
		threo	erythro
$Ca_3(PO_4)_2$	300	89 (88)	85 (84)
	400	88 (81)	85 (82)
BPO_4	165	55 (56)	45 (46)
	300	48 (49)	52 (49)
$Ba_3(PO_4)_2$	330	72 (71)	66 (66)
	460	73 (71)	73 (71)
$CaHPO_4$	305	71 (70)	66 (67)
	340	72 (70)	67 (68)
$AlPO_4$	290	45 (46)	45 (44)
	400	52 (51)	48 (49)

Over BPO_4 the E1 mechanism is preferred and therefore the calculation of the E2 mechanisms has only formal character.

Because of decomposition of $CaHPO_4$ above 350°C only the range of temperature below 100% conversion was investigated. Over $Ba_3(PO_4)_2$ the temperature of 100% conversion is 450°C. The percentage of E2 remains practically constant in the range of conversion and no dependence of temperature can be observed over these two catalysts.

Over $AlPO_4$ the E1 mechanism is low and syn E2 and anti-E2 are similar. The corrected and the previously calculated mechanisms are practically equal.

In principle, the correction of the former calculation of E2 mechanisms can be applied to all catalysts. In practice, high syn E2 or anti-E2 preference gives the possibility to account for the influence of E1 percentage upon E2 mechanisms. This is the case with $Ca_3(PO_4)_2$.

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