over $MgSO_4$ and concentrated. The remaining oil produced under vacuum solid sulfoximide, 0.43 g (46%), which was recrystallized from ethyl acetate at −78° to give 0.26 g of the hygroscopic sulfoximide **5**.

Thiane-1-(*N*-tosyl)imide 1-Oxide (8). Tosyl chloride (2.15 g) and thian-1-imide 1-oxide (**5**, 0.75 g) were stirred in 30 ml of dry pyridine at room temperature for 24 hr. Water was added, and the mixture was extracted with $CHCl_3$. Evaporation of the $CHCl_3$ produced a yellow liquid, to which toluene was added in order to remove the pyridine as an azeotrope. The volume was reduced in this manner to about 5 ml. Concentration under reduced pressure left a white solid, which was recrystallized from ethyl acetate to give 1.2 g (75%) of white crystals, mp 136–137°. *Anal.* Calcd for $C_{12}H_{17}NO_3S_2$: C, 50.17; H, 5.92; N, 4.87. Found: C, 50.04; H, 6.00; N, 4.87.

Tracer Studies of Acid-Catalyzed Reactions. XI. Stereoselectivity in Alcohol Dehydration over Hydroxyapatite and Alumina Catalysts

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Abstract: The reactions of model compounds (*threo-* and *erythro*-2-butanol-*3-d*$_1$ and *cis-* and *trans*-2-methylcyclohexanol) were used to characterize the surfaces of alumina and calcium-deficient hydroxyapatite catalysts. Over alumina, the butenes formed by dehydration contained the following percentages of the monodeuterated molecules: 94% of the 1-butene, 80% of the *trans*-2-butene, and 28% of the *cis*-2-butene from the threo stereoisomer and 94, 28, and 84%, respectively, from the erythro compound. Over hydroxyapatite, the corresponding results were 95, 29, and 74% for the threo, and 95, 80, and 39% for the erythro stereoisomer. Thus, anti elimination was the preferred mode over alumina and syn elimination over hydroxyapatite. The results from the cyclohexanols were not so straightforward. Anti elimination by both catalysts was indicated for *cis*-2-methylcyclohexanol. The ratio of 1-methylcyclohexene to 3-methylcyclohexene found for hydroxyapatite (3.0) was in good agreement with that reported by Pines and Blanc for alumina. With the trans isomer, however, the ratio for hydroxyapatite (1.1) was much higher than that reported for alumina (0.14–0.37). With both catalysts, the cis isomer reacted a little faster than the trans, and 25–35% of the deuterium from *trans*-2-methylcyclohexanol-*2-d*$_1$ was retained in the 1-methylcyclohexene product. Over hydroxyapatite, the kinetics were zero order in reactant and activation energies were about 26 and 30 kcal/mol, respectively, for methylcyclohexanol and 2-butanol. Saytzeff elimination was favored over Hofmann with both catalysts.

Several studies of the stereospecificity of alcohol dehydration to olefins over metal oxide catalysts have been made.[2–4] Pines and coworkers found that the olefin product distributions in dehydration of primary and secondary alcohols over alumina approached those expected for a concerted anti elimination.[2,3] It was proposed that dehydration takes place in pores or crevices in the alumina surface, with the alcohol molecules situated between an acidic site on one surface and a basic site on another. Lundeen and Van Hoozer,[4] however, showed that dehydration of secondary alcohols over a thoria catalyst occurred mainly *via* syn elimination, and that Hofmann elimination was strongly favored over Saytzeff. They suggested that these results stemmed from stringent steric requirements which they envisioned for formation of the transition state with their system, but noted that strong carbanion character in the transition state would favor Hofmann elimination.

Dehydrations of primary and secondary alcohols over hydroxyapatite (basic calcium phosphate) catalysts yielded olefin product distributions which were similar to those obtained in dehydrations of the corresponding alcohols over alumina,[5] except that the cis/trans ratios tended to be lower. The hydroxyapatite used was not porous; its surface area was made up almost entirely by crystal faces.[6] Consequently, there was very little possibility of anti elimination in crevices as proposed for alumina. Moreover, the low selectivity for 1-alkene formation from secondary 2-alkanols over hydroxyapatite suggested that should syn elimination be found, the reaction could not be comparable with that on thoria.

The present paper concerns an attempt to use the reactions of model alcohols to describe properties of the catalyst surface, *e.g.*, the nature of the catalytic sites and of the transition state. It was hoped that the rapidly growing knowledge of these matters in homogeneous media could be translated to this end. The reader should recognize, therefore, that it was not our purpose to debate the controversial mechanistic points. Data are presented confirming that anti elimination predominates over alumina and showing that syn elimination is favored with 2-butanol over hydroxyapatite. Complete stereospecificity was not achieved, however, over either catalyst.

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Experimental Section

Materials. *cis*- and *trans*-2-methylcyclohexanol were obtained from K&K Chemical Co. and purified by gas chromatography. *trans*-2-Methylcyclohexanol-*2*-d_1 was prepared by deuterioboration of 1-methylcyclohexene (K&K Chemical Co.), followed by oxidation with hydrogen peroxide.[7] The required B_2D_6 was generated by the reaction of BF_3 with $NaBD_4$ (Merck Sharp and Dohme; quoted as 98% D). The product was purified by gas chromatography; *ca.* 2% *cis*-2-methylcyclohexanol and 0.5% 1-methylcyclohexanol impurities remained. Mass spectrometric analysis of 3-methylcyclohexene formed by dehydration of the *trans*-2-methylcyclohexanol-*2*-d_1 gave 12% d_0 and 88% d_1, implying an isotopic purity of >88%. (Blanc and Pines[3] found >84% d_1 using $LiAlD_4$ to introduce deuterium into *trans*-2-methylcyclohexanol.)

threo- and *erythro*-2-butanol-*3*-d_1 were prepared in a similar way.[8] *trans*-2-Butene and *cis*-2-butene (both Lif-O-Gen >99% pure) were deuterioborated and purified by gas chromatography. Since the threo and erythro isomers could not be separated, the conformational purities were determined by the method of Skell and Hall.[9] The acetates were prepared and the isotopic compositions of the butenes formed on pyrolysis were determined mass spectrometrically. The acetates were prepared by reaction of the alcohols with acetyl chloride in dimethylaniline. After purification by gas chromatography (to remove traces of methyl chloride), each acetate was pyrolyzed by passing the vapor in a carrier flow of helium through a tube containing crushed glass maintained at 450°. High flow rates (low conversions) were used to minimize isomerization of the olefins formed. Nmr spectra of the two alcohols confirmed that the conformational purities exceeded 90%.

Catalysts. The preparation of the hydroxyapatite catalyst has been described.[6] In the present work a 150-mg sample of a calcium-deficient preparation (Ca/P atom ratio = 1.58) was used; its specific surface area was 46 m^2/g. Before each run it was pretreated in flowing dry helium at 500° for 15–20 hr before introducing sufficient H_2O into the heated stream to provide a partial pressure of about 300 Torr. The latter (1 hr) treatment was made because it was found previously[5] that this restored the catalyst to its maximum dehydration activity. The preparation and properties of the alumina have been given elsewhere.[10–14] A 27-mg sample was pretreated in a flow of dry helium at 500° for 15–20 hr, and then in oxygen at 500° for 1 hr, before each run. Its specific surface area was 310 m^2/g.

Apparatus. A continuous flow of reactant was passed over the catalyst in a microcatalytic system.[15] A sampling valve allowed a portion of the product mixture to be diverted to a chromatograph column which separated the olefins from unreacted alcohol. The column packings were diglycerol on Chromosorb P, used at 120° for the methylcyclohexanols, and polypropylene glycol on the same carrier, used at 85° for the 2-butanols. The olefin fractions were trapped for analysis on a second column. Methylcyclohexenes were separated on a silver nitrate–ethylene glycol column, and the butene separations were made with a methylsulfolane column, both operating at 0°. Each component of the olefin mixtures from runs with deuterated alcohols was trapped and passed through the appropriate column repeatedly, until it was free of the other isomers; it was then analyzed for deuterium content on a Nuclide 6-in. 60° magnetic sector mass spectrometer using low (~10 eV) ionizing voltages.

Results

Dehydration of 2-Methylcyclohexanols over Hydroxyapatite. When *cis*- or *trans*-2-methylcyclohexanol was allowed to react over hydroxyapatite between 250 and 350°, the major olefin products (comprising over 90% of the total) were 1-methylcyclohexene and 3-methylcyclohexene. Below 300° traces (1–2% each) of 4-methylcyclohexane and methylenecyclohexane were also formed. The relative amounts of these minor products increased slightly above 300° where two additional products appeared. These were vinylcyclopentane and ethylidenecyclopentane, which made up 4% of the total olefin product at 350°.

Over hydroxyapatite, the reaction was zero order in alcohol at partial pressures between 10 and 50 Torr. The activation energy of the reaction was 26–27 kcal/mol for both alcohols, but *cis*-2-methylcyclohexanol was dehydrated at a rate which was about 20% faster than that of the trans isomer. No isomerization of 3-methylcyclohexene, 4-methylcyclohexene, or the cyclopentanes occurred, but 1-methylcyclohexene and methylenecyclohexane were readily interconverted. Therefore, the product ratios involving 1-methylcyclohexene were determined at low alcohol conversions, so as to reflect the initial values.

The ratios of 1-methylcyclohexene to 3-methylcyclohexene in products from dehydration of *cis*-2-methylcyclohexanol are given in Table I; the corresponding ratios for *trans*-2-methylcyclohexanol are listed in Table II. Also included (values in parentheses) are the available data for the dehydration of the 2-meth-

Table I. Dehydration of *cis*-2-Methylcyclohexanol over Alumina and Hydroxyapatite Catalysts

	Product ratio[a,b]		Reciprocal temp, $10^3/T$, °K^{-1}
Catalyst	*R*	ln *R*	
Alumina[c]	3.1	1.13	1.61
	3.0	1.10	1.75
	3.5	1.25	1.91
	3.8 (2.65)	1.34 (0.98)	1.95
	4.0 (3.0)	1.39 (1.10)	2.05
Hydroxy-apatite[d]	2.7	1.00	1.61
	3.1	1.14	1.65
	3.2	1.15	1.71
	3.2	1.16	1.71
	3.0	1.11	1.71
	3.1	1.14	1.75
	3.2	1.15	1.79
	3.8	1.34	1.83

[a] *R* = 1-methylcyclohexene/3-methylcyclohexene. [b] Values in parentheses are for the *2*-d_1 alcohol. [c] Data taken from ref 3. [d] Present work.

Table II. Dehydration of *trans*-2-Methylcyclohexanol over Alumina and Hydroxyapatite Catalysts

	Product ratio[a,b]		Reciprocal temp, $10^3/T$, °K^{-1}
Catalyst	*R*	ln *R*	
Alumina[c]	0.3	−0.99	1.61
	0.23	−1.46	1.75
	0.14	−1.95	1.91
	0.19	−1.68 (−1.67)	1.95
	0.14	−1.97 (−1.84)	2.05
Hydroxy-apatite[d]	1.25 (1.25)	0.22 (0.22)	1.65
	(1.07)	(0.07)	1.69
	1.19 (1.06)	0.17 (0.06)	1.75
	1.10 (1.12)	0.09 (0.11)	1.81
	1.18	0.17	1.93

[a] *R* = 1-methylcyclohexene/3-methylcyclohexene. [b] Values in parentheses are for the *2*-d_1 alcohol. [c] Data taken from ref 3. [d] Present work.

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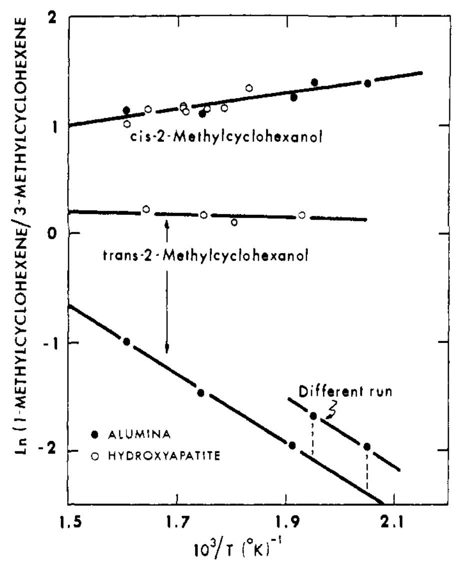


Figure 1. Product ratios from dehydration of two model alcohols.

ylcyclohexanols-*2*-d_1. Comparison is made with the data of Blanc and Pines[3] for alumina catalysts in these tables and both sets of data are plotted in Figure 1.

The deuterium contents of 1-methylcyclohexene and 3-methylcyclohexene, produced in the dehydration of *trans*-2-methylcyclohexanol-*2*-d_1 over hydroxyapatite, were determined to be 30 and 88%, respectively. Assuming that deuterium was not lost in the formation of 3-methylcyclohexene, the isotopic purity of the alcohol was 88%, and 34% of the deuterium label was retained in the formation of 1-methylcyclohexene.

Pyrolysis of Butyl Acetates. In order to determine the conformational purity of the alcohols, the acetates of the *threo*- and *erythro*-2-butanol-3-d_1 were pyrolyzed at 450°. The distributions of the *n*-butenes produced are compared in Table III with results of Skell and Hall[9] for the reaction at 400°. Listed in this table, also, are the isotopic compositions of the butene isomers from each pyrolysis. The 1-butene data are a measure of the isotopic purity. After correcting for the amounts of unlabeled 2-butenes which arise from unlabeled acetate, the isotopic compositions of the 2-butenes are then a measure of the conformational purity.

Table III. Pyrolysis of *threo*- and *erythro*-2-Butyl-*3*-d_1 Acetates

	Relative yields			
Acetate	1-Butene	*trans*-2-Butene	*cis*-2-Butene	
A. Butene Product Distributions at 400 and 450° (Normalized)				
Threo *3*-d_1	1.000	0.309	0.299	This work, 450°
Erythro *3*-d_1	1.000	0.500	0.172	
Threo *3*-d_1	1.00	0.30	0.28	Ref 9, 400°
Erythro *3*-d_1	1.00	0.49	0.15	Ref 9, 400°
Normal (d_0)	1.00	0.49	0.26	Ref 9, 400°
B. Isotopic Composition of Butene Products at 450°				
Threo *3*-d_1	95[a,c]	10 (4)[a,c]	91 (94)[a,c]	
Erythro *3*-d_1	94[a,c]	93 (97)[a,c]	4.3 (3)[a,c]	
Threo *3*-d_1	100[b,c]	11[b,c]	96[b,c]	
Erythro *3*-d_1	100[b,c]	99[b,c]	4.9[b,c]	

[a] Data of ref 9 in parentheses. [b] Corrected, assuming all 1-butene-d_0 is from acetate-d_0 and that *trans*- and *cis*-2-butenes from acetate-d_0 are formed in the ratios of 0.50 and 0.30, respectively, relative to 1-butene-d_0. [c] Per cent monodeuterated.

Isotope effects operate in two ways in this reaction. In the absence of a conformational impurity, the cis/trans ratio is altered in favor of the d_1 isomer, *i.e.*, more *cis*- or *trans*-2-butene-d_1 is formed from the threo or erythro conformer, respectively, relative to *trans*- or *cis*-2-butene-d_0, and the ratio changes accordingly. This effect is evident in the data of Table III. When one conformer is present as an impurity in the other, the isotope effect operates with both to increase the relative amount of the monodeuterated product. Thus, the apparent anti elimination product of the principal acetate will actually be formed by syn elimination of the impurity, and the percentage of this product will vary depending upon whether it is monodeuterated or undeuterated.

Skell and Hall[9] showed that pyrolysis of the acetates of *threo*- and *erythro*-2-butanol-*3*-d_1 within experimental error yielded only the syn elimination products (100 ± 3%). Pyrolysis of the acetate of the threo alcohol yielded (Table III) 11% *trans*-2-butene-d_1 and 3.8% *cis*-2-butene-d_0 (syn elimination products of the erythro isomer). The acetate of the erythro alcohol yielded 4.9% *cis*-2-butene-d_1 and 1.4% *trans*-2-butene-d_0 (syn elimination products of the threo isomer). The kinetic isotope effect, k_H/k_D, favoring loss of hydrogen *vs.* loss of deuterium, was estimated from these data. The ratio, d_1/d_0, in the trans product of the threo alcohol and the ratio, d_0/d_1, in the cis product can be equated by correcting for the isotope effect, *i.e.*, $11k_D/89k_H = 3.8k_H/96k_D$ or $k_H/k_D = 1.8$. For the erythro acetate the corresponding values were $99k_D/1.4k_H = 95k_H/4.9k_D$ or $k_H/k_D = 1.9$. Adopting an average value of 1.85, ratios of product coming from the principal alcohol and from its impurity can be calculated; for the threo alcohol this ratio is $(89 \times 1.85)/11 = 15$ and for the erythro alcohol it is $(95 \times 1.85)/4.9 = 46$. These ratios can be converted readily to per cent purity; these are 94% for the threo and 98% for the erythro alcohol.

Dehydration of 2-Butanols over Hydroxyapatite and Alumina. The only reaction products were the three *n*-butenes. The product distributions were similar over the two catalysts (Tables IV and V); more *cis*-

Table IV. Dehydration of 2-Butanol-d_0, *threo*-2-Butanol-*3*-d_1, and *erythro*-2-Butanol-*3*-d_1 over Calcium-Deficient Hydroxyapatite at 310°

	Relative yields			Ratios[a]	
Alcohol	1-Butene	*trans*-2-Butene	*cis*-2-Butene	1B/2B	Cis/trans
A. Butene Product Distribution (Normalized)					
Threo *3*-d_1	1.00	0.56	1.28	0.54	2.25
Erythro *3*-d_1	1.00	0.67	1.17	0.54	1.76
Normal (d_0)	1.00	0.78	1.41	0.46	1.81
B. Isotopic Composition of Butene Products					
Threo *3*-d_1	95[b]	29[b]	74[b]		
Erythro *3*-d_1	95[b]	80[b]	39[b]		
Threo *3*-d_1	100[b,c]	38[b,c]	78[b,c]		
Erythro *3*-d_1	100[b,c]	85[b,c]	42[b,c]		

[a] 1B/2B is the ratio of 1-butene to 2-butenes. Cis/trans is the ratio of *cis*-2-butene to *trans*-2-butene. [b] Per cent monodeuterated. [c] Corrected assuming all of 1-butene-d_0 is from 2-butanol-d_0 and that ratios of *trans*-2-butene-d_0 and *cis*-2-butene-d_0 to 1-butene-d_0 are 0.78 and 1.41, respectively, from 2-butanol-d_0.

Table V. Dehydration of 2-Butanol-d_0, *threo*-2-Butanol-3-d_1, and *erythro*-2-Butanol-3-d_1 over Alumina at 200°

Alcohol	Relative yields: 1-Butene	Relative yields: *trans*-2-Butene	Relative yields: *cis*-2-Butene	Ratios[a]: 1B/2B	Ratios[a]: Cis/trans
A. Butene Product Distributions (Normalized)					
Threo 3-d_1	1.00	0.40	1.90	0.44	4.75
Erythro 3-d_1	1.00	0.30	2.61	0.34	8.7
Normal (d_0)	1.00	0.40	2.59	0.33	6.6
B. Isotopic Composition of Butene Products					
Threo 3-d_1	94[b]	80[b]	28[b]		
Erythro 3-d_1	94[b]	28[b]	84[b]		
Threo 3-d_1	100[b,c]	85[b,c]	30[b,c]		
Erythro 3-d_1	100[b,c]	35[b,c]	89[b,c]		

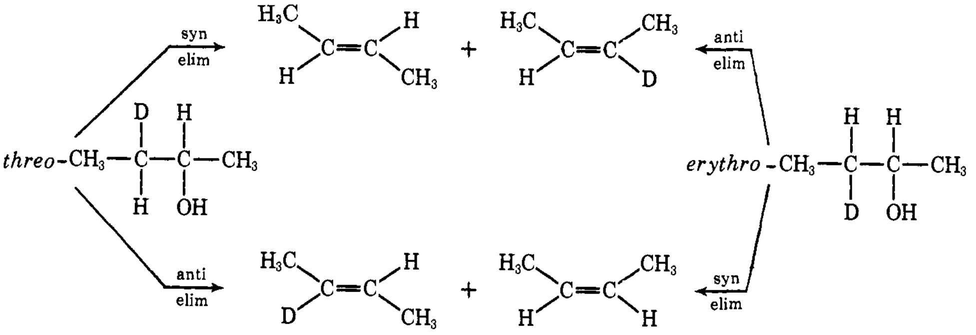
[a] 1B/2B is the ratio of 1-butene to 2-butenes. Cis/trans is the ratio of *cis*-2-butene to *trans*-2-butene. [b] Per cent monodeuterated. [c] Corrected assuming all of 1-butene-d_0 is from 2-butanol-d_0 and that ratios of *trans*-2-butene-d_0 and *cis*-2-butene-d_0 to 1-butene-d_0 are 0.40 and 2.59, respectively, from 2-butanol-d_0.

2-butene was formed than 1-butene and more of the latter than the trans isomer. Over hydroxyapatite, the dehydration was zero order with respect to the alcohol and the activation energy was 30 kcal/mol; no isomerization of the butene products occurred at 310°. Over alumina, the kinetics were not as simple; in particular, alumina is an effective catalyst for butene isomerization, and ether formation is also possible. At the temperature used and for low alcohol conversions (high-flow rates), no ether formation was observed and isomerization of the product olefins was minimal (note high cis/trans ratios). The relative yields and isotopic compositions of the butene isomers formed from the threo alcohol, the erythro alcohol, and unlabeled 2-butanol are also given in these tables, where the last two rows give the values corrected for the amount of unlabeled alcohol present in the starting material. It is evident that syn elimination is favored over hydroxyapatite and anti over alumina.

From the data in Tables IV and V, the rates of formation of the various isotopic 2-butenes, relative to the rate of formation of 1-butene-d_1, may be calculated for both labeled alcohols and both catalysts. These relative rates of formation are listed in Table VI.

Discussion

Dehydration of 2-Butanols. *threo*- and *erythro*-2-butanol-3-d_1 provide a test of the preferred mode of elimination, *i.e.*



The observable quantity is the type of product formed, not the conformation on the surface. Syn elimination products are formed when the groups are removed from the same side of the molecule and anti elimination products when the groups are removed from the opposite side. The former should be normal for surface catalyzed reactions and the latter for reactions in solution.

Table VI. Dehydration of *threo*- and *erythro*-2-Butanol-3-d_1 over Hydroxyapatite and Alumina Catalysts

	Relative rates of formation: Hydroxyapatite catalyst[a]: Threo alcohol	Hydroxyapatite catalyst[a]: Erythro alcohol	Alumina catalyst[b]: Threo alcohol	Alumina catalyst[b]: Erythro alcohol
1-Butene-d_1	1.000	1.000	1.000	1.000
trans-2-Butene-d_0	0.382	0.097	0.060	0.205
trans-2-Butene-d_1	0.173	0.565	0.340	0.089
cis-2-Butene-d_0	0.281	0.680	1.206	0.278
cis-2-Butene-d_1	0.987	0.483	0.643	2.332

[a] At 310°. [b] At 200°.

The data of Tables IV–VI show that 2-butanol dehydration is mainly a syn elimination on the hydroxyapatite surface, and mainly an anti elimination on the alumina, but that the reaction is not completely stereospecific on either. The kinetic isotope effects are evidenced by the higher percentages of monodeuterated 2-butenes formed. Loss of deuterium from 2-butanol-3-d_1 is expected to be slower than loss of hydrogen from unlabeled alcohol (primary isotope effect); also, loss of hydrogen from the 3 position of 2-butanol-3-d_1 may be either faster or slower than from the unlabeled alcohol (secondary isotope effect). The rate of formation of 1-butene, however, should be very nearly the same for all three 2-butanols. Normalizing these rates to unity, the relative rates of formation of the 2-butenes from the unlabeled 2-butanol are

$$\text{rate t2B } (\textit{trans}\text{-2-butene}) = k_t^{a} + k_t^{s} \tag{1}$$

$$\text{rate c2B } (\textit{cis}\text{-2-butene}) = k_c^{a} + k_c^{s} \tag{2}$$

where k_i^j is the relative rate of formation of isomer i (cis or trans) by j elimination (syn or anti). The rates of formation of the monodeuterated 2-butenes, which involve only secondary isotope effects, are for the threo alcohol

$$\text{rate t2B-}d_1 = 0.94 r_t k_t^{a} + 0.067 r_t k_t^{s} \tag{3}$$

$$\text{rate c2B-}d_1 = 0.94 r_c k_c^{s} + 0.067 r_c k_c^{a} \tag{4}$$

and for the erythro alcohol

$$\text{rate t2B-}d_1 = 0.98 r_t k_t^{s} + 0.026 r_t k_t^{a} \tag{5}$$

$$\text{rate c2B-}d_1 = 0.98 r_c k_c^{a} + 0.026 r_c k_c^{s} \tag{6}$$

where r_t and r_c are secondary isotope effects (k_D/k_H), assumed to be insensitive to the mode of elimination. From eq 1–6, values for the secondary isotope effects and (relative) rate constants were calculated for both catalysts from the data in Table VI; the results are listed in Table VII. The secondary isotope effects were small and, within experimental error, may be taken as unity.

Table VII. Dehydration of 2-Butanol over Hydroxyapatite and Alumina. Stereospecificity and Kinetic Isotope Effects

	Catalyst[b]	
	Hydroxy-apatite	Alumina
Relative rates[a]		
k_t^a	0.16	0.322 (81%)
k_t^s	0.620 (80%)	0.073
k_c^a	0.44	2.13 (82%)
k_c^s	0.96 (71%)	0.46
Isotope effects (k_H/k_D)		
$1/r_t$	1.1	0.9
$1/r_c$	0.9	0.9
$1/R_t^a$	1.7	1.5
$1/R_t^s$	1.5	1.5
$1/R_c^a$	1.7	1.7
$1/R_c^s$	1.4	1.8

[a] Relative to 1-butene. [b] Values given in parentheses are the percentages of the reaction which follow the stereoselective pathway.

The rates of formation involving primary isotope effects are, for the threo alcohol

$$\text{rate t2B} = 0.94R_t^s k_t^s + 0.067R_t^a k_t^a \qquad (7)$$

$$\text{rate c2B} = 0.94R_c^a k_c^a + 0.067R_c^s k_c^s \qquad (8)$$

and for the erythro alcohol

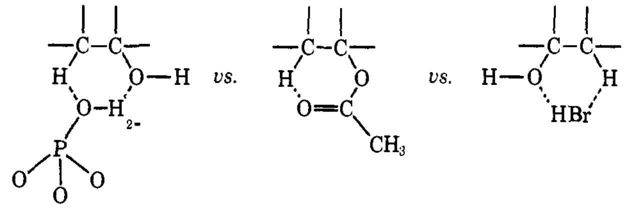
$$\text{rate t2B} = 0.98R_t^a k_t^a + 0.026R_t^s k_t^s \qquad (9)$$

$$\text{rate c2B} = 0.98R_c^s k_c^s + 0.026R_c^a k_c^a \qquad (10)$$

where the R's are primary isotope effects, k_D/k_H, associated with the corresponding relative rate constants. Using eq 7–10, the values for the k's obtained from eq 1–6, and the data in Table VI, the primary isotope effects were calculated for both catalysts. These are also given in Table VII. They were similar for both catalysts, varying from 1.4 to 1.8. The differences among the data were not large enough, in view of the possible uncertainties (*ca.* 10%), to be considered very significant.

The syn elimination over hydroxyapatite was unusual in that the cis/trans ratio exceeded unity. In homogeneous reactions more *trans-* than *cis*-2-butene is usually formed (*e.g.*, Table III) because of the unfavorable steric interaction between the two methyl groups in the required eclipsed configuration. Consequently, high cis/trans ratios are usually associated with anti elimination processes. (Note that $k_c^s/k_t^s = 1.6$ compared with $k_c^a/k_t^a = 2.9$.) The high ratios found in the present case suggest that specific steric requirements imposed by the catalyst surface may be more important than those within the molecule.

Ionic (E1) reactions are not stereoselective. The mode of elimination (syn or anti) in concerted homogeneous reactions depends on properties of the reaction system and mainly on those of the substrate molecule. Syn elimination occurs from eclipsed configurations of the molecule, anti from gauche. Since the latter are lower in energy, anti elimination will be preferred except in those circumstances where special interactions exist which favor eclipsing, *e.g.*, in acetate pyrolysis[7] or the gas-phase catalysis of dehydration by HBr.[16–20] In these cases cyclic transition states have been proposed and a similar one may be postulated for hydroxyapatite, *i.e.*



The data of Table IV indicate that while the dehydration over hydroxyapatite was mainly syn elimination, the reaction was not as stereoselective as reactions in homogeneous media. In the latter case, it is easy for the molecules to take on the preferred configurations leading to complete stereospecificity. When a surface is involved, the hydroxyl group of the alcohol must bond to an acidic center and a β hydrogen must be discharged to a basic center. These interactions may stabilize the transition state in rotational configurations different from those required in homogeneous media, and this may modify the results. Thus, two different centers (rather than the single POH pictured above) could function, and the expanded system could now utilize some of the gauche configurations. This would result in loss in stereoselectivity.

Anti elimination is favored over alumina. The cause for this may be associated with the surface structure. If the alcohol adsorbs with its OH covering an exposed aluminum ion, both the alcoholic hydrogen and alkyl group should be directed away from the surface. A factor which is usually overlooked is that the basic center (the O^{2-}), which must accept the β hydrogen, is also covering an aluminum ion on a nearby site and has a size comparable with the adsorbed molecule. Thus, the β hydrogen atoms which are directed away from the surface can interact more easily with the top of the basic centers than those at the bottom of the molecule.

The fixed geometry of the surface places constraints on the transition states which are absent in homogeneous media. In the latter, the acid and base can approach the substrate from all directions and the lowest energy pathway leads to complete stereoselectivity. In the heterogeneous reaction, compromises have to be made and complete stereoselectivity cannot be expected. Nevertheless, the results do provide considerable insight into the nature of the surface sites and the mechanism of the reaction. Although it is not yet certain, the present results suggest that anhydride or dual Lewis acid–base surfaces will effect anti elimination while weak Brønsted systems, which catalyze the reaction through a cyclic intermediate, will lead to syn elimination.

Dehydration of 2-Methylcyclohexanols. Blanc and Pines[3] studied the dehydration of *cis-* and *trans*-2-

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(16) A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 2836 (1960).
(17) K. G. Lewis and V. R. Stimson, *ibid.*, 3087 (1960).
(18) R. A. Ross and V. R. Stimson, *ibid.*, 3090 (1960).
(19) E. J. Watson and V. R. Stimson, *ibid.*, 3920 (1960); 1392 (1961).
(20) R. L. Failes and V. R. Stimson, *ibid.*, 653 (1962).

methylcyclohexanol over an alumina catalyst. The major olefin products were 1-methylyclohexene and 3-methylcyclohexene, both of which may be formed by β elimination of water. The same products were formed when these alcohols were allowed to react over hydroxyapatite. As shown in Table I, the 1-MCH–3-MCH ratios from *cis*-2-methylcyclohexanol were almost identical for the two catalysts; the data can be represented by the same line on an Arrhenius plot (Figure 1). The difference in activation energy for formation of the two products was not very large ($\sim$1.5 kcal/mol), and it favored the formation of 1-MCH.

The product ratios obtained from dehydration of *trans*-2-methylcyclohexanol over the two catalysts were quite different. Over alumina they varied between 0.14 and 0.37 (Table II), as compared with 3–4 for the cis alcohol, and they changed rapidly with temperature (Figure 1). Over hydroxyapatite, the ratios were only a little lower for the trans alcohol (1.1–1.3) than for the cis (2.7–3.8) and they did not vary appreciably with temperature (Figure 1). The fact that the product ratios were quite different for the two alcohols over both catalysts rules out the possibility that a common carbonium ion intermediate was formed along the reaction coordinate from both alcohols.

Pines and coworkers[2,3] interpreted their data for alumina as a preferred anti elimination. With *cis*-2-methylcyclohexanol-*2-d*$_1$, the deuterium atom was selectively removed in the formation of the preferred product, 1-methylcyclohexene, and a normal kinetic isotope effect was observed (Table I). With *trans*-2-methylcyclohexanol, 3-methylcyclohexene was the preferred product, presumably because only it can be formed directly by anti elimination. When this substrate was deuterium labeled in the 2 position, 25% of the product 1-methylcyclohexene retained its deuterium and no kinetic isotope effect was observed for its formation (Table II). Blanc and Pines eliminated the possibility that this secondary product resulted from a concerted syn elimination on the grounds that specific loss of deuterium with a normal isotope effect was not found with the trans as it was with the cis alcohol. Hence, they concluded that this product stemmed from an E1 process or from a concerted reaction with γ participation.

Similar results were obtained in the present work for the hydroxyapatite catalyst. About 30% of the deuterium label was retained in the 1-methylcyclohexene product from the trans alcohol and the kinetic isotope effect was not appreciable for 1-methylcyclohexene formation (Table II). As with alumina, it does not appear that the formation of 1-methylcyclohexene can be explained by a concerted syn elimination even though this product was formed faster over hydroxyapatite than 3-methylcyclohexene. Therefore, with both catalysts a major product was formed from the trans alcohol by some mechanism other than a simple β elimination. Moreover, since deuterium was retained, either the methyl group or the deuterium atom must have moved in this process. These results agree in detail with those reported by Schaeffer and Collins[21] and by Price, *et al.*,[22,23] for the 2-phenylcyclohexanols dehydrated in H_3PO_4. The cis compound yielded 1-phenylcyclohexene very selectively, but extensive phenyl migration occurred when this product was formed from the trans alcohol. Also, benzylcyclopentane and 1-benzylcyclopentene were major products from the latter. Schaeffer and Collins[21] were able to rationalize these results quite satisfactorily by arguments based on the structure of the two distinct chair conformations available to each alcohol. Thus, three totally different catalyst systems, H_3PO_4, alumina, and hydroxyapatite, produced remarkably similar results with the substituted cyclohexanols. This carries over even to the distribution of the minor products (4-methylcyclohexane, methylenecyclohexane, vinylcyclopentane, and ethylidenecyclopentane). Thus, the present work adds little to our knowledge of the mechanisms of these reactions and the reader is referred to earlier discussions of this question.[2,21–24]

The data of Tables IV and V show that anti elimination from the 2-butanols is favored over alumina, but that syn elimination is the dominant pathway over hydroxyapatite. This raises the question as to why syn elimination is not the preferred pathway with *trans*-2-methylcyclohexanol over hydroxyapatite. The rate of syn elimination is strongly dependent upon the dihedral angle formed between the tetrahedra centered on the carbon atoms α and β to the OH group. With the butanols, the angle can readily approach its optimum value (zero) by forming the cyclic transition state; with the cyclohexanols, this can be accomplished only if the molecule is converted into the boat configuration which lies higher in energy. Thus, it would appear that structural considerations within the methylcyclohexanol molecules control the course of the reaction. If so, these molecules cannot be as useful in characterizing properties of the surface as the butanols.

Just as anti elimination is expected to be the rule in homogeneous media (in the absence of special circumstances), geometric constraints would be expected to require syn elimination for surface-catalyzed reactions. Thus, to explain anti elimination over alumina, Pines, *et al.*,[2,3] suggested that the alcohol molecules reacted in small pores between two surfaces. This cannot be the explanation for the reaction over hydroxyapatite. This catalyst was comprised of small individual nonporous crystals[6]; cracks large enough to accommodate cyclohexanol molecules did not exist in measurable quantities. A possible alternative is suggested by the Peri model[25] of the alumina surface. Here the dual acid–base sites are aluminum ions, exposed where the terminal OH groups are missing, and *large* O^{2-} ions replacing the OH groups and covering adjacent lattice positions. If it is assumed that the alcoholic hydroxyl group covers the aluminum ion with the alcoholic hydrogen pointing away from the surface, hydrogen atoms on the β carbon atom in the trans position to the hydroxyl group can be discharged on top adjacent O^{2-} ions more readily than those in the cis positions. This is because the size of the O^{2-} is about the same as

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[21] H. G. Schaeffer and C. J. Collins, *J. Amer. Chem. Soc.*, **78**, 124 1956).

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that of a methane molecule. This geometry may be readily confirmed with scale models. The most probable configuration appears to be one where the cyclohexane ring is in the chair form, stands at an angle with the plane of the surface, and discharges the β hydrogen from the backside of the molecule. Thus, the *deep* crack or crevice envisioned by Pines is evidently not required. Something similar must be envisaged for hydroxyapatite.

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σ–π Conjugation Effects in the Acid Cleavage of Allylmercuric Halides

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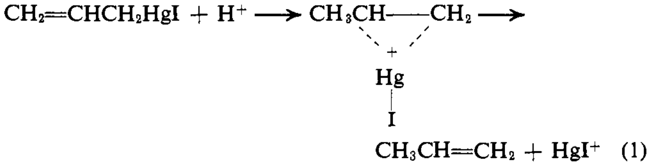
Abstract: Extended Hückel molecular orbital calculations suggest that the minimal energy conformation of allylmercuric bromide has the carbon–mercury bond perpendicular to the nodal plane of the olefinic π system resulting in delocalization of the double bond. A unique reaction pathway for the acid cleavage of allylmercuric halides is described. The extent of σ–π stabilization in the transition state for this cleavage reaction is shown to depend upon the conformation of the allylmercuric halide, the hybridization at the allylic carbon atom, and the polarizability of the carbon–mercury bond.

Organometallic compounds containing an allyl group bonded to a metal often exhibit enhanced reactivity toward electrophilic reagents. For example, allylmercuric iodide is rapidly cleaved by aqueous perchloric acid affording propene.[1] This reaction is some six orders of magnitude faster than the hydration of propene,[2] although both reactions involve attack of proton on the carbon–carbon double bond. This unusual reactivity has been attributed[3] to the extensive involvement of the mercury in the transition state of the reaction. The rate-determining step in allylmercuric iodide cleavage by aqueous acid has been shown by kinetic studies to be proton transfer to carbon. Kinetic isotope effects suggest that the reaction coordinate does not involve large components of heavy atom motions.[1b] Solvent effects on the ultraviolet spectra of allylmercuric iodide have led to the suggestion[3] that the ground state of this molecule exists in a conformation that can readily form an olefin–mercuric iodide π complex which closely resembles the transition state for this protolysis reaction (eq 1). To accommodate this mechanism the mercury atom must be rotated approximately 90° out of the nodal plane of the double bond in the ground state. Allyltin and other allylmetallic compounds are also cleaved by acid at rates that are markedly in excess of the rate of protonation of propene.[4a] It has been established for some time that the R_3MCH_2 group (M = Si, Ge, Sn) has a greater electron-releasing capacity than the R_3M group.[4b] This effect is often cited as evidence for pπ–dπ bonding and more recently has been attributed in part to hyperconjugation of the carbon–metal bond (σ–π conjugation).[4c–e] Stabilizaton of neighboring cationic centers by carbon–metal bonds has also been involved with benzylmercury halides,[5a,b] α-ferrocenyl carbonium ions,[5c–e] and in the formation of cyclopropanes from 3-tosyloxyalkyltrimethyltin.[5f] A variety of spectroscopic evidence also has been reported that supports a ground-state interaction between the σ C–M bond and an allylic double bond.[6a–d] The concept of σ–π conjugation, and the requirement that the C–M bond and the axis of the electron-deficient π orbital must be coplanar, has recently been demonstrated by Traylor[5e,7] and Pitt.[8]



$$\mathrm{CH_2{=}CHCH_2HgI} + \mathrm{H^+} \longrightarrow \underset{\substack{+ \\ \mathrm{Hg} \\ | \\ \mathrm{I}}}{\mathrm{CH_3CH{-}{-}CH_2}} \longrightarrow \mathrm{CH_3CH{=}CH_2} + \mathrm{HgI^+} \quad (1)$$

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