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Catalytic Conversion of Alcohols

XXVIII. Product Selectivities for 2-Methylcyclohexanol Conversion with Metal Oxide Catalysts

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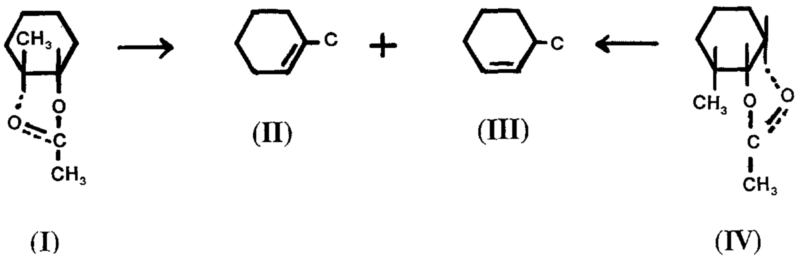
Metal oxides exhibit a range of selectivities (dehydration percentage, alkene distribution and alcohol isomerization) for the conversion of a 2-methylcyclohexanol isomer. For many metal oxide catalysts, *trans*-2-methylcyclohexanol produces a predominance of the less stable 3-methylcyclohexene isomer. The grouping of metal oxides based on the production of the less stable alkene isomers from 2-octanol is similar to that for *trans*-2-methylcyclohexanol. It is proposed that the same catalytic properties determine the selectivity for both reactants: for smaller metal cations the product selectivity is determined by steric crowding in the transition state, and for the larger cations the product selectivity is determined by the basicity of the oxygen anion and the relative acidity of the β-hydrogens that are eliminated to produce water.

INTRODUCTION

The nature of the active sites in a heterogeneous catalyst is of vital interest. In any catalytic reaction an intermediate is formed by a combination of reactant molecule(s) and the active site. Unfortunately, it is a rare instance when the chemical character of the active site is well defined. To write a mechanism under these conditions requires much speculation.

Chemists have made extensive use of stereochemistry to help unravel reaction mechanisms (*1*). Reactants that have been frequently utilized include *cis*- or *trans*-2-methylcyclohexanol or similar compounds (*2*). Thus, organic chemists were able to show that pyrolysis of the acetate ester of an alcohol predominately followed a *syn* elimination mechanism (*3*a,b).

In this instance 1-methylcyclohexene **(II)** is the more stable alkene product and is expected to be formed in larger amounts when the mechanism is dominated by the stability of the products, as would be expected for an E-1 mechanism. For *trans*-2-methylcyclohexyl acetate **(I)**, both products **(II and III)** may be formed by a *syn* elimination mechanism; experimentally, it is observed that the more stable isomer, 1-methylcyclohexene, comprises 80–90% of the products. For the other isomer, *cis*-2-methylcyclo-



(I) (II) (III) (IV)

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hexyl acetate (**IV**), the most stable alkene, **II**, cannot be formed by a *syn* elimination mechanism, and experimentally it is observed that the less stable product, **III**, comprises ca. 90% of the products. Thus, acetate pyrolysis is shown to follow an E-2 mechanism that involves *syn* elimination to form acetic acid and methylcyclohexene.

With an acidic catalyst, such as amorphous silica–alumina, the alkene products from the conversion of an alcohol consist of essentially an equilibrium distribution, and even some C–C chain isomerization may occur, as would be expected from an E-1 type (carbocation) type mechanism. With a less acidic alumina catalyst, *anti* elimination is the dominant reaction pathway (*4*). Thus, it was shown that the *trans* alcohol isomer produced predominantly the less stable isomer, **III**.

Pines and Manassen (*5*) believe that the mechanism for dehydration in alumina involves pores that are sufficiently narrow for elimination of water to occur in a concerted process where the OH is eliminated by bonding to one side of the pore, while at the same time the *anti*-H is eliminated by bonding to the opposite pore wall. Schmidtmeyer and Moffat (*6*) have utilized this reactant to investigate the nature of the catalytic site in Al–P–O catalysts and have reviewed some of the earlier catalytic studies with this reactant (*7–14*).

In view of the stereospecific nature of reactions involving 2-methylcyclohexanol it is desirable to define the course of the dehydration of this alcohol with a number of oxide catalysts that show a range of selectivities for the dehydration of 2-octanol (*15*). By comparing the product from the conversion of *cis*- and *trans*-2-methylcyclohexanol isomers, it should be possible to place metal oxide catalysts between the extremes of the elimination pathways, *syn* or *anti* elimination. The results of such a study are the subject of this article.

EXPERIMENTAL

Most of the catalysts were prepared by precipitation of the hydrous metal oxide from a metal nitrate solution with ammonium hydroxide (Table 1). More detailed descriptions of the preparation of particular catalysts can be found in earlier publications of this series. The hydrous metal oxide, following extensive washing, was dried in air at 120°C, and then calcined at 500 or 600°C in air. Prior to use as a catalyst, the metal oxide was pretreated *in situ* in either air, oxygen, or hydrogen at 500°C as indicated in the tables of data.

Conversion was effected in a plug flow reactor fitted with a thermowell extending to the center of the catalyst bed. About 20–30 mL of the reactor volume above the catalyst bed contained Pyrex glass beads to serve a preheater. Liquid products were collected at room temperature at increasing time intervals. Selectivity data are reported for samples collected during a "steady-state" period following the initial contact of the catalyst with the alcohol reactant.

The alcohol isomers were obtained from Wiley Organics and were used without further purification. In general, the alcohol purity was >99% (GC analysis).

Products were identified by GC–MS, and reaction products were monitored by GC. The extent of conversion to alkene and ketone was measured using a Carbowax 20 column. Alkene distributions were obtained using a DB-5 capillary GC column. *cis*- and *trans*-2-Methylcyclohexanol compositions were obtained using a diglycerol column.

RESULTS AND DISCUSSION

The alcohol conversion pathways include as primary reactions: (1) dehydration by a *syn* or *anti*-concerted pathway or by a carbonium ion or "carbanion," (2) *cis*/*trans* isomerization of the reactant alcohol, and (3) dehydrogenation to ketone. These reaction pathways for the alcohol isomers are summarized below:

1. Alcohol Isomerization

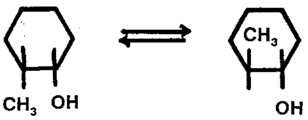


TABLE 1

Preparative Procedure and Surface Areas for Metal Oxide Catalysts

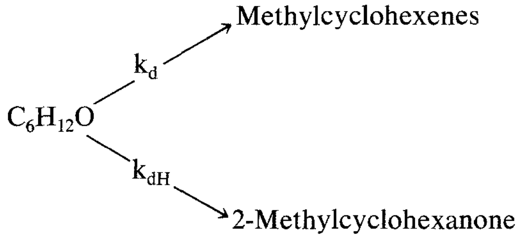
Material	Salt	Precipitating agent	Surface area (m^2/g)	Reference
Al_2O_3-A	isopropoxide	H_2O	210	(*20*)
Al_2O_3-K	potassium aluminate	CO_2	190	(*20*)
Ga_2O_3	nitrate	NH_4OH (pH ~ 7)	52.3	(*8*)
WO_3[a]	ammonium tungstate	HNO_3	20[a]	(*18*)
HfO_2	nitrate	NH_4OH (pH ~ 10)	32	(*10*)
$Hf_{0.6}Zr_{0.4}O_2$	mixed nitrate salts	NH_4OH (pH ~ 10)	36	(*16*)
ZrO_2	nitrate	NH_4OH (pH ~ 10)	42	(*9*)
ThO_2(Cl)	chloride	NH_4OH (pH ~ 7)	24	(*19*)
$ThO_2(NO_3)$	nitrate	NH_4OH (pH ~ 7)	42	(*19*)
UO_3[b]	nitrate	NH_4OH	[b]	(*24*)
Cr_2O_3	nitrate	NH_4OH	20	(*24*)
Gd_2O_3	nitrate	NH_4OH	28	(*24*)
ZnO	nitrate	NH_4OH	—	(*24*)
Fe_2O_3	nitrate	NH_4OH (pH ~ 8)	37	(*22*)
Eu_2O_3	nitrate	NH_4OH (pH ~ 10)	32.5	(*24*)
Y_2O_3	nitrate	NH_4OH	46.4	(*17*)
TiO_2	nitrate	NH_4OH	46.1	(*11*)
Nd_2O_3	nitrate	NH_4OH	32.8	(*21*)
MgO(2)[c]	oxide	—	—	(*23*)
CaO[c]	oxide	—	—	(*23*)

[a] Area after calcining at ca. 400°C; oxide is reduced by the alcohol during use and area of working catalyst is not known.

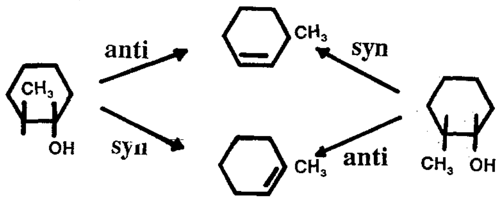
[b] Oxide is reduced by the alcohol during use; area of working catalyst is not known.

[c] MgO or CaO was converted to the hydroxide by immersion in water, the hydroxide collected by filtration, and the hydroxide converted to the oxide *in situ*.

2. Dehydration/Dehydrogenation



3. Alkene Selectivity (for concerted elimination)



A carbonium ion mechanism, and most carbanion mechanisms, will form a common intermediate from each alcohol; hence, in these cases olefin distributions are not useful in defining a reaction mechanism. In addition to the chemical selectivities imparted by the geometry of the reactant and/or reaction mechanism, catalyst pretreatment (hydrogen vs. oxygen) may impact, in many cases, one or more of the selectivities. Results that are representative of the product selectivities are summarized in Table 2 for the conversion of *cis*-2-methylcyclohexanol and in Table 3 for the *trans* isomer.

An undesirable selectivity is the result of secondary isomerization reactions of the alkenes, e.g.,

TABLE 2

Conversion of *cis*-2-Methylcyclohexanol

	Temp.	Pretreatment	Conv. (%)[a]	Alkene products[b]	Trans (%)[c]	3-Methyl-cyclohexene[d]	Isomerization[e]
Al_2O_3	180	O_2 (450)	34	>.99	0	81	0
Ga_2O_3	240	air	55.8	0.99	trace	6.1	—
WO_3	252	oxygen	39.0	0.98	trace	13	—
HfO_2	270	air	19.6	0.99	0.71	18	0.04
	270	H_2	18.4	0.99	0.85	21	0.04
$Hf_{0.6}Zr_{0.4}O_2$	235	air	9.4	0.89	.82	16	0.08
ZrO_2	250	air[f]	11.8	0.33	39.6	57	0.77
	250	H_2	10.4	0.39	35.5	49	0.77
ThO_2(Cl)	250	H_2 (500)	12.1	0.88	2.2	12	0.15
UO_3	350	air	9.3	0.66	1.01	27	0.10
	360	H_2	14.5	0.41	30.3	48	0.68
Cr_2O_3	180	air	17.2	0.76	trace	22	~0
CaO	348	air	39.2	0.78	7.6	24	0.16
Gd_2O_3	220	air	31.2	0.81	42.2	83	0.57
	250	air	17.9	0.73	27.9	60	0.61
ZnO	282	air	6.4	0.01	11.0	34	0.63
Fe_2O_3	200	air	19	0.99	~0.0	11	~0.0
Eu_2O_3	250	air	11.4	0.40	15.7	34	0.58
$ThO_2(NO_3)$	250	H_2 (500)	6.5	0.88	19.4	70	0.75
Y_2O_3	285	H_2	23.7	0.10	68.1	38.4	0.74
Nd_2O_3	300	air	5.8	0.19	32	30	0.63
TiO_2	250	air	22.8	0.94	0.49	24	0.02

[a] Alkene and ketone formed.
[b] Alkene/(alkene + ketone).
[c] *trans* Alcohol/total alcohol.
[d] 3-Methylcyclohexene/methylcyclohexenes.
[e] *trans* Alcohol/*trans* alcohol + alkene + ketone.
[f] >90 1-octene from 2-octanol.

It was shown that this latter reaction was usually not significant provided conversion of the alcohol was kept low (30%), so that the relative pressure of the alcohol was high enough to ensure surface coverage by the alcohol (*25*).

The dehydration selectivity is compared to the ability of the catalyst to effect isomerization and dehydrogenation. The pathway represented is

$$\begin{tikzcd}
 & \text{Alkene + ketone} \\
\text{Alcohol isomer} \arrow[ur] \arrow[dr] & \\
 & \text{Other alcohol isomer.}
\end{tikzcd}$$

The dehydration selectivity is defined as the ratio [alkene/(alkene + ketone)], while the isomerization selectivity for the above scheme can be defined as the ratio [other alcohol isomer/(alkene + ketone)]. Reactant isomerization and dehydrogenation may be independent reactions; that is, a catalyst may effect isomerization without catalyzing the dehydrogenation reaction and vice versa. For this reason we have plotted dehydration selectivity versus alcohol interconversion defined as [alcohol isomerized / (alkene + ketone)] in Figs. 1 and 2, and 3-methylcyclohexene selectivity versus alcohol interconversion in Figs. 3 and 4. While this definition of alcohol interconversion differs from isomerization as defined in Tables 2 and 3, it is preferred for these figures since

TABLE 3

Conversion of *trans*-2-Methylcyclohexanol

	Temp.	Pretreatment	Conv. (%)[a]	Alkene[b]	*cis* (%)[c]	3-Methyl cyclohexene[d]	Isomer (%)[e]
Al_2O_3	180	O_2 (450)	32	~1.0	0	24	0
Ga_2O_3	240	air (500)	6.5	~1.00	1.70	66	~0
WO_3	260	air	29	~1.00	~0	32	~0.0
	260	Hydrogen/H_2O	10	~1.00	~0	36	~0.0
HfO_2	270	air	4.1	>0.97	0.3	46	0.07
	270	H_2	5.9	>0.97	0.1	—	0.01
$Hf_{0.6}Zr_{0.4}O_2$	240	air	5.3	0.91	0.22	44	0.04
ZrO_2	250	air (500)	9.0	0.54	9.91	57	0.52
	250	H_2 (500)	7.38	0.51	9.28	60	0.56
$ThO_2(Cl)$	250	H_2 (500)	0.67	0.6	1.17	31	0.64
UO_3	355	air (500)	10.0	0.12	2.43	46	0.20
	355	H_2 (500)	5.7	0.60	9.6	62	0.63
Cr_2O_3	180	air (450)	4.6	0.40	1.8	57	.28
MgO(2)	340	air (500)	14.5	0.81	6.32	47	0.30
	336	H_2 (500)	28.9	0.29	29.0	47	0.50
CaO	350	air	22.3	0.60	9.26	37	0.29
	350	H_2	21.2	0.64	21.9	40	0.51
Gd_2O_3	220	air	41.0	0.32	8.6	93	0.17
	250	air	22.6	0.35	9.24	83	0.29
ZnO	310	air	28	0.01	19	39	0.40
	298	H_2 (500)	51	0.02	26	42	0.34
Fe_2O_3	200	air	24	0.99	~0	52	~0.0
Eu_2O_3	250	air (500)	6.8	0.46	5.7	77	0.46
$ThO_2(NO_3)$	250	H_2 (500)	4.0	0.40	3.86	86	0.49
Y_2O_3	298	H_2 (500)	22.3	0.12	34	56	0.60
Nd_2O_3	300	air (525)	4.2	0.21	8.3	61	0.66
TiO_2	250	air (500)	24	0.99	0.7	35	0.03

[a] Conversion to alkene and ketone.
[b] Alkene/alkene + ketone.
[c] *cis*-Alcohol/*cis* + *trans* alcohol.
[d] 3-methylcyclohexene/methylcyclohexenes.
[e] *cis* Alcohol/*cis* alcohol + alkene + ketone.

it emphasizes alcohol interconversion verus these other selectivities. Furthermore, the dehydration selectivity and alcohol isomerization conversion is being compared on a common basis; the denominator in both cases is (alkene + ketone). For comparative purposes, this is preferred to graphing on the basis of total conversion. Furthermore, the equilibrium limitations of the *cis–trans* alcohol conversion prohibits us from making an accurate measure of the molecules isomerized for very selective isomerization catalysts; this makes a valid comparison of this reaction to the irreversible dehydration and dehydrogenation reactions based on total conversion is questionable. Thus, while the abscissa in Figs. 1–4 are identified as *cis* or *trans* alcohol isomerized, the reader should realize that the equilibrium condition limits the ability to measure the number of molecules isomerized for those catalysts active enough to approach an equilibrium composition (*trans*/*cis* ~2).

In making the comparison a range of temperatures have been utilized since the activity of the many metal oxides vary over a wide range. We have made many runs with an alcohol over one sample of a particular metal oxide catalyst, as well as many runs in which we have utilized a variety of prepa-

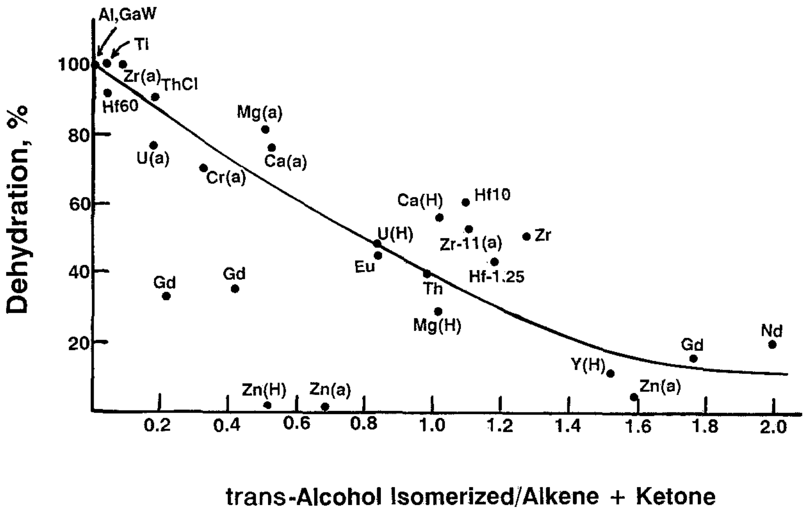


FIG. 1. The dehydration selectivity [alkene/(alkene + ketone)] × 100 versus the alcohol isomerization activity [*cis* alcohol/(alkene + ketone)] for the conversion of *trans*-2-methylcyclohexanol with metal oxide catalysts [(a), air pretreatment; others are for hydrogen pretreatment].

ration and activation procedures with a common reactant. Thus, the data in Tables 2 and 3 as well as Figs. 1–6 represent steady state conversion data for a particular run. Certain metal oxides do not have a selectivity that strongly depends upon preparation (e.g., MoO_3) whereas others (e.g., ThO_2) show selectivities that strongly depend upon preparation and pretreatment. As a result, there may be slight differences in the data between the tables and the figures due to use of data from different runs. In fact, in some figures, more than one selectivity may be plotted as, for example, Gd(a) in Fig. 3. In spite of this, the general trends remain valid. Similar trends are observed with each reactant isomer. In general, catalysts that exhibit significant capability for alcohol

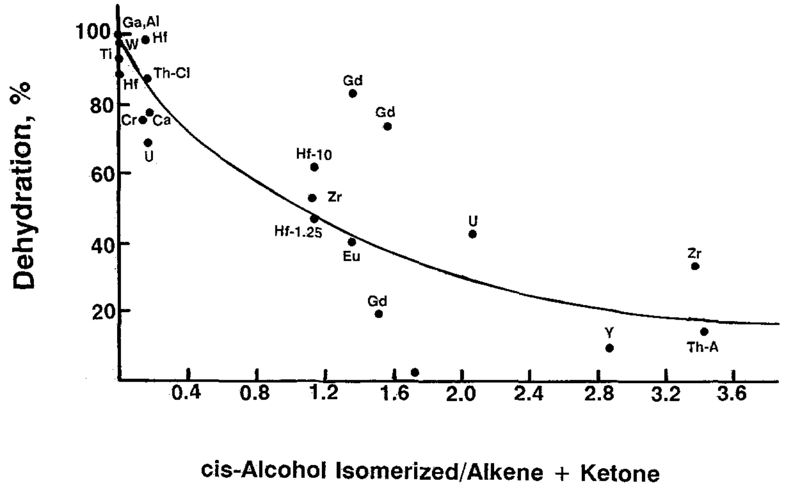


FIG. 2. The dehydration selectivity [alkene/(alkene + ketone)] × 100 versus the alcohol isomerization activity [*trans* alcohol/(alkene + ketone)] for the conversion of *cis*-2-methylcyclohexanol with metal oxide catalysts [(a), air pretreatment; others are for hydrogen pretreatment].

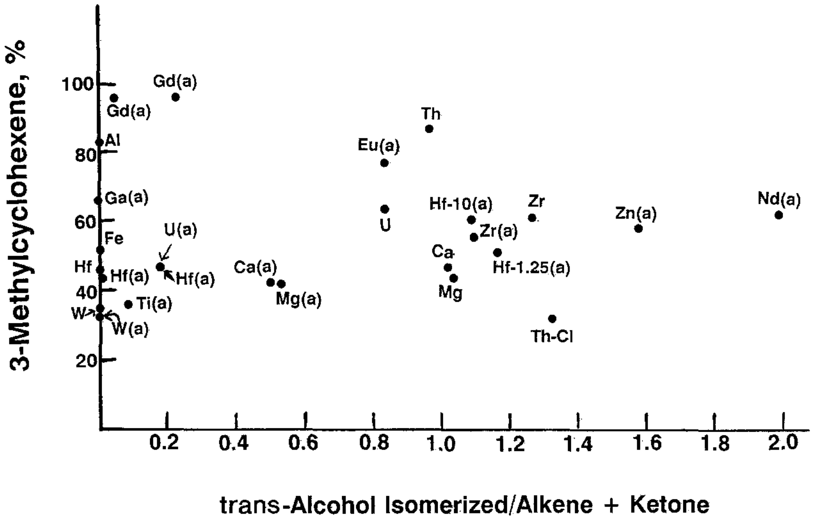


FIG. 3. The percentage of alkene fraction represented by the less stable isomer, 3-methylcyclohexene, versus alcohol isomerization activity [(a), air pretreatment; others are for hydrogen pretreatment] for the conversion of *trans*-2-methylcyclohexanol.

isomerization also show lower selectivity for dehydration. ZnO departs significantly from the trend, since it is very selective for alcohol dehydrogenation but is not as active for isomerization compared to other oxides. Gd_2O_3 also appears to depart from the trend since it catalyzes dehydrogenation to a greater extent than anticipated for its *cis* ↔ *trans* isomerizing activity. Furthermore, Gd_2O_3 appears to be quite sensitive to preparation and/or pretreatment conditions, so that in some cases it appears to be even more selective for dehydration than anticipated from the general trend (Fig. 2).

It has been established that the Meerwein–Pondorff–Verley reaction readily occurs over the metal oxides used in this study. For example, for the conversion of a

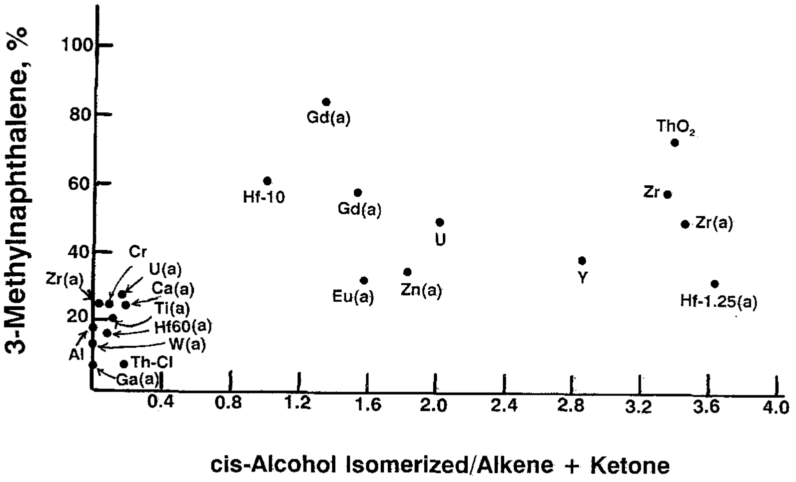
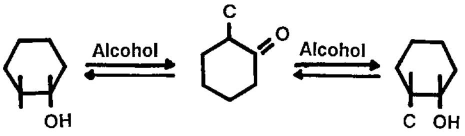


FIG. 4. The percentage of alkene fraction represented by the less stable isomer, 3-methylcyclohexene, versus alcohol isomerization activity [(a), air pretreatment; others are for hydrogen pretreatment] for the conversion of *cis*-2-methylcyclohexanol.

mixture of 2-butanone and 2-octanol, or vice versa, the Meerwein–Pondorff–Verley reaction occurs at least as rapidly as alcohol dehydration (*24*). Thus, *cis* ↔ *trans* isomerization of 2-methylcyclohexanol is considered to involve the Meerwein–Pondorff–Verley reaction so that isomerization occurs through a ketone intermediate,



Alumina, for example, is found to be a very active catalyst for this reaction (*26–28*). The reason for the absence of *cis* ↔ *trans* alcohol isomerization during alcohol conversion with alumina and those other catalysts with a high dehydration selectivity is that the concentration of ketone needed for the isomerization reaction is too small.

Further support for the isomerization being a Meerwein–Pondorf–Verley type of reaction was obtained by a comparison of the conversion data for *cis*- or *trans*-2-methylcyclohexanol and their corresponding methyl ethers (*29*). When a reactant mixture of an isomeric alcohol and its corresponding methyl ether were converted over a metal oxide catalyst, e.g., yttria, both compounds underwent the elimination reaction to produce methylcyclohexene. During the conversion of the alcohol and ether mixture, the alcohol underwent dehydrogenation to the ketone and *cis* ↔ *trans* isomerization while the ether, which cannot undergo dehydrogenation to the ketone, did not undergo *cis–trans* isomerization.

For dehydration, a common intermediate is not formed from the *cis* and *trans* isomers. The alkene distribution from the two geometric alcohol isomers would be identical if a common intermediate was formed, and this is not the case. Thus, even in most cases where *cis* ↔ *trans* alcohol isomerization occurred, different alkene compositions were obtained.

TABLE 4

Fraction of 3-Methylcyclohexene in the Alkene Products Formed from *trans*-2-Methylcyclohexanol with Metal Oxides that are Selective Dehydration Catalysts

Products	3-Methylcyclohexene (%)[a]
Al_2O_3	82
Ga_2O_3	66
Fe_2O_3	52
HfO_2	46
TiO_2	35
WO_3	32

[a] Percentage of 3-methylcyclohexene isomer in the alkene products.

The first grouping of metal oxide catalysts to be considered are those that are a very selective (>95%) dehydration catalyst and are essentially inactive for alcohol isomerization. The fraction of the dehydration products that correspond to an *anti* elimination mechanism is catalyst-dependent within a group of metal oxides that are very selective dehydration catalysts (Table 4). Thus, alumina produces alkenes that indicate a strong preference for anti-elimination. On the other hand, tungsten oxide (air pretreated) is a very selective dehydration catalyst that produces similar, but not identical, products from the *cis* and *trans* alcohol (Figs. 3 (*trans* isomer) and 4 (*cis* isomer)). For dehydration of *cis*-2-methylcyclohexanol with tungsten oxide, the more stable alkene, 1-methylcyclohexene, corresponds to 87% of the alkene products. For *trans*-2-methylcyclohexanol dehydration, 68% of the alkene fraction was the more stable alkene, 1-methylcyclohexene. For WO_3, the extent of *cis* ↔ *trans* isomerization of the alcohol reactants is exceptionally low; thus, the alkene product is not impacted by reactant isomerization in this case, or for the other metal oxides that are selective dehydration catalysts.

The data in Table 4 indicate that for metal oxides that are selective dehydration catalysts the extent of anti-elimination decreases in the order

$$Al_2O_3 > Ga_2O_3 > Fe_2O_3 > HfO_2 > TiO_2 > WO_3.$$

These differences in selectivity do not appear to be due to a secondary isomerization of the alkene products. For Ga_2O_3, Fe_2O_3, and TiO_2, 1-octene did not undergo significant conversion to 2-octene when it was passed over the catalyst together with 2-methylcyclohexanol.

The catalysts in a second grouping of metal oxides exhibit a unique alkene selectivity. The less stable alkene, 3-methylcyclohexene, is the dominant product for the conversion of either the *cis*- or *trans*-2-methylcyclohexanol reactant. An extreme example of this second group is illustrated in Fig. 5 by the data obtained for Gd_2O_3. With *trans*-2-methylcyclohexanol, the amount of the alkene obtained from an anti-elimination mechanism is greater than 90%. Surprisingly, the amount of the less stable alkene product is ca. 80% for *cis*-2-methylcyclohexanol conversion. The data for the conversion of these two alcohols with Gd_2O_3 also differ in two other aspects: (1) the selectivity for dehydration is ca. 80% for the *cis* alcohol but only ca. 35% for the *trans* isomer, and (2) the *cis* alcohol undergoes isomerization to the *trans* isomer more rapidly than the *trans* alcohol isomerizes to the *cis* alcohol. The total alcohol conversion (dehydrogenation plus dehydration) is ca. 30% for the *cis* alcohol and 40% for the *trans* alcohol. In the experiment to generate the data shown in Fig. 5 the Gd_2O_3 a sample was pretreated in air at 500°C and then flushed with nitrogen. First, *cis*-2-methylcyclohexanol was passed over the catalyst and then, after collecting four samples, the reactant feed was switched to *trans*-2-methylcyclohexanol and, after ca. 30 min., four samples were collected (Fig. 5). Thus, both reactants were exposed to the same metal oxide that had identical pretreatment and reaction conditions. These surprising results are therefore not due to variations in the metal oxide used to convert the alcohols or to its pretreatment. Another portion of the Gd_2O_3 sample, after activation in either hydrogen or air at 500°C, was selective for producing 1-octene (>90%) from 2-octanol; the dehydration selectivity was 41% for the air-pretreated sample and 50% for the hydrogen-pretreated material.

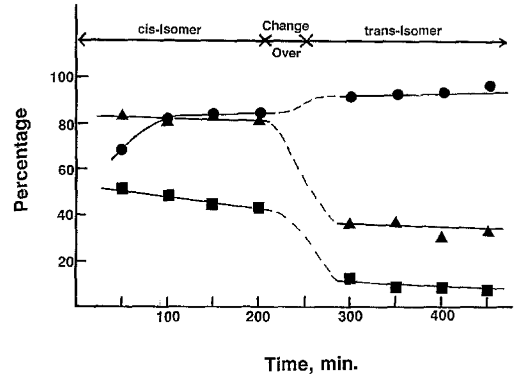


FIG. 5. The percentage of products represented by less stable alkene [3-methylcyclohexene × 100/methylcyclohexenes; ●], dehydration [alkenes × 100/(alkenes + ketone), ▲], and alcohol isomerization (■) for the conversion of *cis*-2-methylcyclohexanol for ca. 200 min followed by flushing with nitrogen and then converting *trans*-2-methylcyclohexanol with Gd_2O_3 at 220°C.

The selectivities for 2-octanol conversion with thorium oxide depend on catalyst preparation and pretreatment (*30*). This dependence on catalyst preparation is also reflected in the data in Table 5. Samples A and B were both prepared by precipitation with ammonium hydroxide; however, they represented two separate preparations. Both samples A and B show similar selectivities for the formation of the less stable alkene, 3-methylcyclohexene, from *cis*- or *trans*-2-methylcyclohexanol. The dehydration selectivity and the activity for alcohol isomerization relative to dehydration plus dehydrogenation are, however, quite different. The catalyst obtained by precipitation from a thorium chloride solution was a selective dehydration catalyst but did not show a strong selectivity for the less stable alkene that is produced by *anti* elimination from *trans*-2-methylcyclohexanol. The catalyst prepared from the thermal decomposition of the carbonate exhibited the highest selectivity for dehydration, exhibited activity for the interconversion of the alcohol isomers,

TABLE 5

Products from the Conversion of 2-Methylcyclohexanol with Thorium Oxide Catalysts

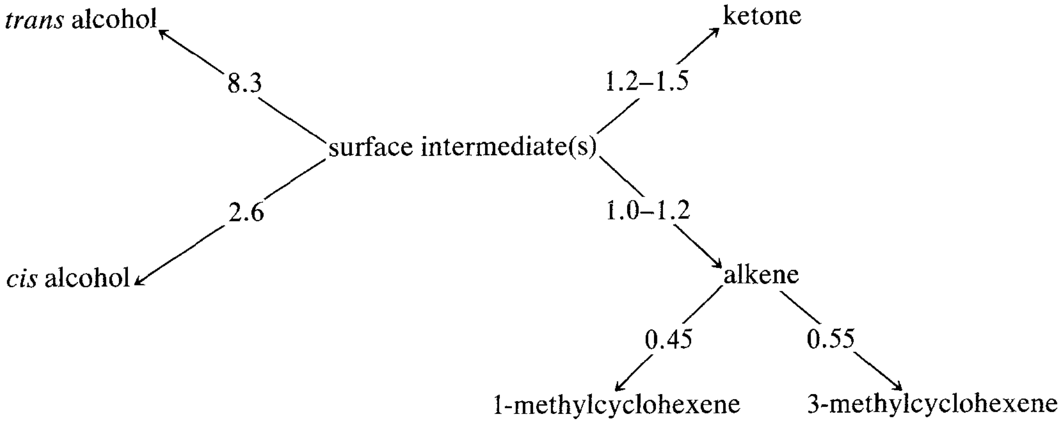
Catalyst	Temp. (°C)	Alcohol	Time (Min)[a]	Conversion (%)[b]	Dehydration (%)[c]	Isomerization (%)[d]	3-Methyl cyclohexene[e]
A (ex-nitrate; H_2, 500°C pretreatment)	250	*trans*	60	4.9	38	3.0	86
			190	4.0	40	3.9	87
A	250	*cis*	70	6.5	18	23	71
			210	5.7	14	19	70
B (ex-nitrate; air, 500°C pretreatment)	285	*trans*	24[f]	54	~98	6.8	83
			27[f]	54	~99	3.2	84
B	280	*cis*	72	55	~98	17	62
			392	53	~97	15	69
C (ex-chloride; H_2, 500°C pretreatment)	250	*trans*	50	1.0	70	2.6	35
			210	0.7	60	1.2	31
C	250	*cis*	60	15	92	7.0	17
			400	11	86	2.2	11
D (ex-carbonate; air, 500°C pretreatment)	280	*trans*	24.5[g]	44	~100	8.5	48
			26.5[f,g]	50	~100	1.7	43
D	280	*cis*	72[f]	70	~98	44	19
			407[f]	58	~99	11	21

[a] Time in hours of exposure to alcohol.
[b] Alkene and ketone formed.
[c] Alkene/(alkene + ketone).
[d] As defined in Tables 1 and 2, depending upon reactant.
[e] 3-Methylcyclohexene/methylcyclohexenes.
[f] 40 mL/min of nitrogen was passed over the catalyst with the alcohol (alcohol partial pressure ca. 0.22).
[g] First 23 hr with 2-octanol only.

and only modest selectivity for anti-elimination from *trans*-2-methylcyclohexanol. The small amount of 3-methylcyclohexene produced from *trans*-2-methylcyclohexanol with thoria obtained from a chloride solution is probably impacted by secondary isomerization of the alkene products; 3-pentanol dehydration over this catalyst produced ca. 10% of 1-pentene even though this isomer cannot be formed directly from this alcohol by a β elimination mechanism. The products from the dehydration of 2-methylcyclohexanol with thoria precipitated from a nitrate solution are essentially primary products since 1-hexene, when passed over the catalyst during the conversion of this alcohol, did not undergo isomerization. Likewise, 1-hexene isomerization was not extensive when it was passed over the thoria derived from thorium carbonate while alcohol was being dehydrated.

A third grouping of metal oxides consists of those that are active catalysts for isomerization of the alcohol reactant. For this group of metal oxides it is not possible to use the amount of 3-methylcyclohexene in the products as a measure of the extent of anti-elimination. Thus, data shown in Tables 2 and 3 may cause a metal oxide catalyst to be placed in this group, even though the dehydration mechanism may be the same as one that applied to the two groups described above.

Zirconia appears to fit in this latter group of metal oxides. Typical selectivities are shown below (*9*); the numbers are relative rates for conversion of the surface intermediate(s) to products:



It is observed that isomerization of the *trans* to the *cis* isomer is more rapid than the dehydration reaction. Hence, conversion of the isomerized reactant molecule prior to desorption could significantly alter the observed alkene distribution from that which would be obtained from the reactant isomer had this isomerization not occurred.

The selectivity for the conversion of 2-octanol with zirconia is very different from that of hafnia (*31*). Furthermore, the alkene selectivities for solid solution mixtures of HfO_2–ZrO_2 appear to be unique. The amount of 1-alkene produced from 2-octanol is ca. 90% for ZrO_2 and remains at that level until the mixture contains 10–15 mole% HfO_2; for HfO_2 content from ca. 10–15 mole% to pure HfO_2, 2-octanol produces only about 35% of the 1-octene isomer. Several surface analytical techniques provided data consistent with a surface composition that corresponds to the bulk composition (*31*); thus, the alkene selectivity changes abruptly with an increase in HfO_2 content. While the change in selectivity is not as dramatic for the conversion of 2-methylcyclohexanol (Table 6), it appears that the selectivities for *trans*-2-methylcyclohexanol conversion also make a rather abrupt change when 10–20 mole% HfO_2 is added to the zirconia. Thus, the dehydration selectivity changes from ca. 60 at 10% HfO_2 to ca. 98% for 20% HfO_2 and higher. The extent of isomerization of the alcohol feed and the

TABLE 6

The Product Distribution from the Conversion of *cis*- or *trans*-2-Methylcyclohexanol with Zirconia, Hafnia, and with Mixed Oxide Catalysts

	cis Reactant			*trans* Reactant		
	Dehydration[a]	3-Me[b]	*Trans* %[c]	Dehydration %	3-Me	*Cis*[d]
ZrO_2	33	57	40	52	60	9.3
90% ZrO_2	—	—	—	60	59	1.1
80% ZrO_2	—	—	—	~98	43	0.55
40% ZrO_2	90	16	0.8	~90	44	0.62
HfO_2	~99	18	0.7	~98	46	0.7

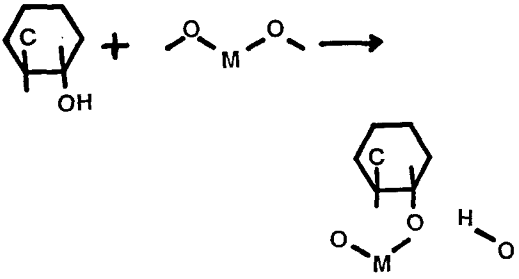
[a] Dehydration/alcohol conversion.
[b] 3-Methylcyclohexene in alkene fraction.
[c] *trans*-2-Methylcyclohexanol/alcohol in product.
[d] *cis*-2-Methylcyclohexanol/alcohol in product.

amount of 3-methylcyclohexene appear to decrease as the HfO_2 content increases.

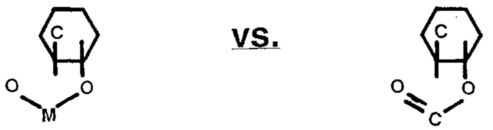
Europia is a selective catalyst for producing 1-octene (>85%) from 2-octanol at 280°C (*24*). Europia has a dehydration selectivity of 40–50% and is an active catalyst for *cis* ↔ *trans* 2-methylcyclohexanol isomerization. However, it appears that elimination by this catalyst occurs predominantly by an anti-mechanism. *trans*-2-Methylcyclohexanol produces ca. 75–80% of the less stable isomer, 3-methylcyclohexene, while the *cis* isomer produces only 30–35% of this alkene, and it is most likely this high because of isomerization of the *cis* alcohol to the *trans* alcohol.

The pyrolysis of esters (acetate and xanthate) of 2-methylcyclohexanol is viewed to follow a highly concerted *syn* mechanism in which little, if any, charge develops. Thus, the ester of the *trans* alcohol, where a *syn* elimination could lead to either 1- or 3-methylcyclohexene, produces predominantly the more stable 1-methylcyclohexene. The ester of the *cis* alcohol can only produce the less stable alkene, 3-methylcyclohexene, by *syn* elimination, and this is the dominant product (*3*).

It is generally accepted that an alcohol adsorbs on a metal oxide by rupture of the OH bond, and IR data show the presence of an alkoxide when an alcohol is adsorbed (*32*). Thus, in the present case we expect adsorption according to the following:

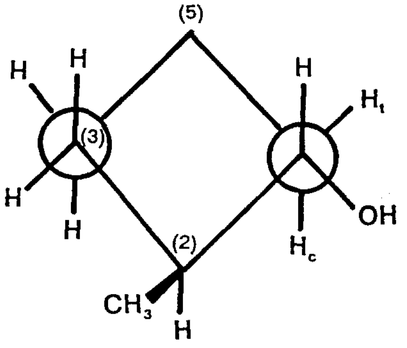


The alcoholate formed upon adsorption in the above reaction can be viewed to be analogous to an ester where the metal, M, has replaced the C in the carboxyl group; i.e.,



Thus, we could anticipate that alcohol dehydration would be analogous to ester pyrolysis. Obviously, this is not the case since the products clearly indicate that alcohol dehydration follows an *anti* mechanism. Thus, the catalytic site or surface must impose restriction upon the reaction mechanism that does not occur in the gas phase pyrolysis.

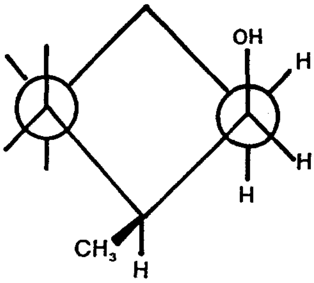
For 2-methylcyclohexanol the most stable conformation should have the chair conformation with the methyl group in an equatorial position. For *trans*-2-methylcyclohexanol this chair conformation, using Newman projections, is shown below,



V

where H_t and H_c represent the hydrogens in the 6 position that are *trans* and *cis*, respectively, with respect to the OH group. [Conventional ring numbering of the ring requires the carbon containing the OH be number 1, the substituent then has the lowest number so that in this case the methyl is attached to carbon number 2; this requires the hydrogen eliminated to form 3-methylcyclohexene be bonded to carbon number 6.] Without steric factors introduced from the metal oxide catalytic site, we should expect about equal loss of H_t and H_c during dehydration to produce 3-methylcyclohexene. Likewise, on a geometric basis the tertiary hydrogen attached to the ring 2 position should be about as susceptible to elimination as H_t. These expectations are not realized.

For *cis*-2-methylcyclohexanol, the following structure applies:



VI

Adsorption of the *cis* isomer as the alkoxide would encounter steric effects due to the CH_3 group and the CH_2 in the ring 4 position. It seems likely that steric factors imposed by the catalytic site cause considerable deviation from the chair conformation, the lowest energy conformation. The heat of chemisorption of an alcohol by a metal oxide catalyst will be considerably more exothermic than the energy barrier leading to ring structures that are considerably distorted from that of the lowest energy chair structure. Thus, the alcohol conversion data indicate that elimination of water from 2-methylcyclohexanol occurs through a transition state with ring structure(s) that are considerably distorted from the lowest energy conformation.

The ionic size of the metal ion is an important factor in determining the selectivity for the condensation of acetone to diacetone alcohol for metal hydroxide catalysts (*33*). A small ionic size is expected to lead to more crowding by the oxygen anion ligands surrounding the adsorption site. The extent of *anti* elimination, judged by the amount of 3-methylcyclohexene formed during dehydration, is plotted versus the ionic size in Fig. 6. With some exceptions, it appears that there is a relationship between the ionic size and the extent of *anti* elimination. For the smaller ionic sizes the selectivity for *anti* elimination of water decreases with increasing ionic radii from ca. 0.5 to 0.7 Å. Most of the metal oxides that fall in this region (Al, Ga, Cr, Fe, Ti) do not catalyze dehydrogenation to an appreciable extent. As the ionic

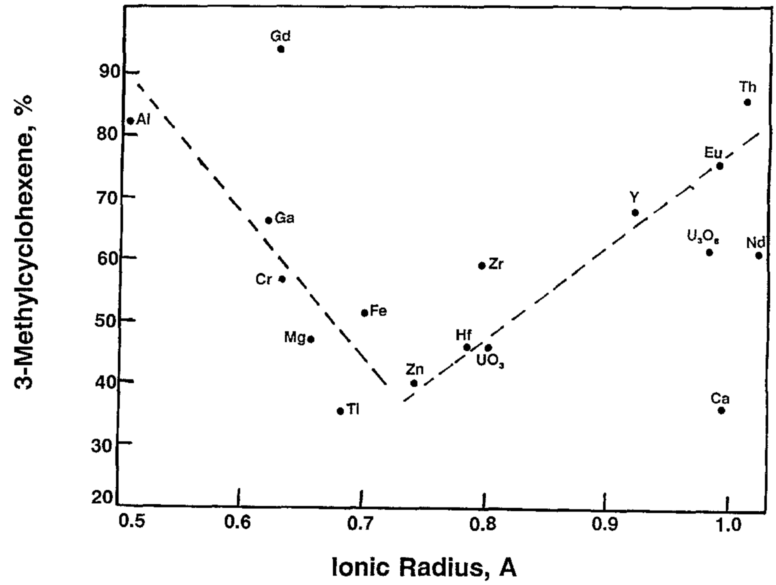
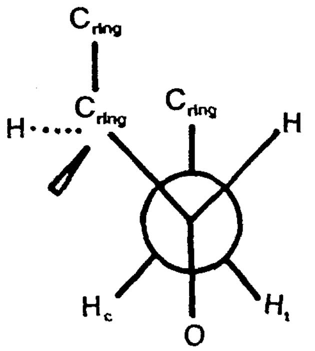


FIG. 6. The percentage of methylcyclohexanes represented by 3-methylcyclohexene versus the ionic radii for the metal cation of oxide catalysts.

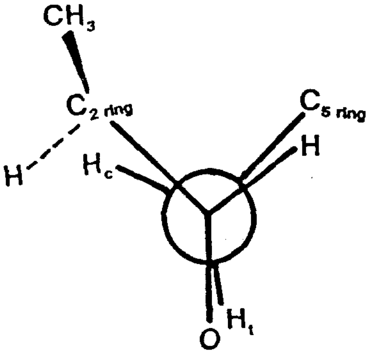
radius increases from ca. 0.7 to 1.0, there is a general increase in the amount of *anti* elimination. Some of the metal ions that have a radius larger than ca. 0.7 may produce a catalyst that is selective for dehydration. For the most part, the metal oxides that are selective for producing a high fraction of 1-alkene from acylic 2-ols have large cations. Thus, there appear to be two general groups of oxides that need to be considered.

The first group of oxides to be considered have ionic radii smaller than ca. 0.7. For adsorption of *trans*-2-methylcyclohexanol, the Newman projection for the chair conformation is



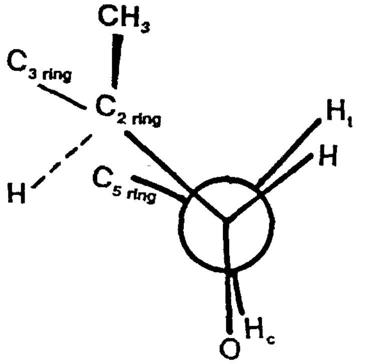
VII

Much of the crowding due to ring and methyl group interactions occur on the left side of the above molecular structure (**VII**); hence, it is not difficult to see how these interactions could distort the above staggered conformation toward the eclipsed conformation (**VIII**) shown below:



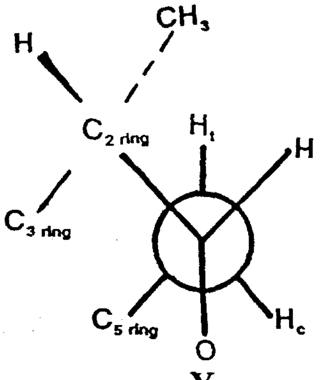
VIII

In this eclipsed conformation the *trans* hydrogen would be the one to be eliminated by a mechanism that resembles the acetate pyrolysis. In the conformation immediately above (**VIII**) the hydrogen *anti* to the OH group is the one that could be eliminated; thus, in this conformation, or conformations closely approaching this eclipsed conformation, the *trans* hydrogen is eliminated by a *syn* mechanism. However, examination of models make it appear that rotation in the other direction about the C_1–C_6 bond would be preferred, even though the methyl group is in an axial position (IX), and the conformation approaches or attains the boat conformation



IX

In this instance a *syn* elimination mechanism results in the loss of the hydrogen *cis* to the OH group. In the case of 2-methylcyclohexanol the ring structure prevents rotation to give a hydrogen on the C_6 carbon in the *anti* position unless the methyl group is placed in an axial position to produce the highest energy conformation (**X**):



X

In this highest energy structure, from the basis of the 2-methylcyclohexanol reactant, an *anti* elimination of H and OH to form water is possible. Irrespective of which of the Newman configurations correctly represents the transition state, it seems likely that the smaller cations have oxygen anions close enough together to provide the steric crowding needed to distort the reactant toward an eclipsed conformation. This small cation-induced crowding would be the driving force toward the higher energy conformational structure of the transition state, and the preference for 3-methylcyclohexene over the more stable 1-methylcyclohexene.

The steric crowding argument will obviously not be applicable for the larger metal cation materials. Many of the oxides that fall in the grouping with metal ion size ca. 0.7 to 1.0 have a high selectivity for producing the 1-alkene from 2-ols. A schematic of the data for 2-octanol conversion from Ref. (*6*) is presented in Fig. 7, together with appropriate identification of metal oxide selectivities. The selectivity for 2-octanol conversion falls into two categories: in one, the two less stable isomers, 1- and *cis*-2-octene, comprise the major products (alumina represents the extreme of this group), and in the other, 1-octene is the dominant product (zirconia represents an extreme of this group). It was proposed that the grouping containing alumina provided steric crowding so that the methyl group of 2-octanol caused the increased production of *cis*-2-octene. In the other grouping it was proposed that base strength dominated in determining the product selectivity, and not steric crowding. For 2-octanol, the base would abstract the more acidic hydrogen in the methyl group to produce 1-octene.

In view of the similarity in the groupings of metal oxides in Figs. 6 and 7, it is inviting to attribute the formation of the less stable alkene, 3-methylcyclohexene in one case and 1-octene in the other, to common catalytic properties. In this connection, it is usual to speak of acid or base properties; however, we realize that one must always have an acid–base pair. Thus, when one refers to increasing base strength, it is *always* implied that the acid component of

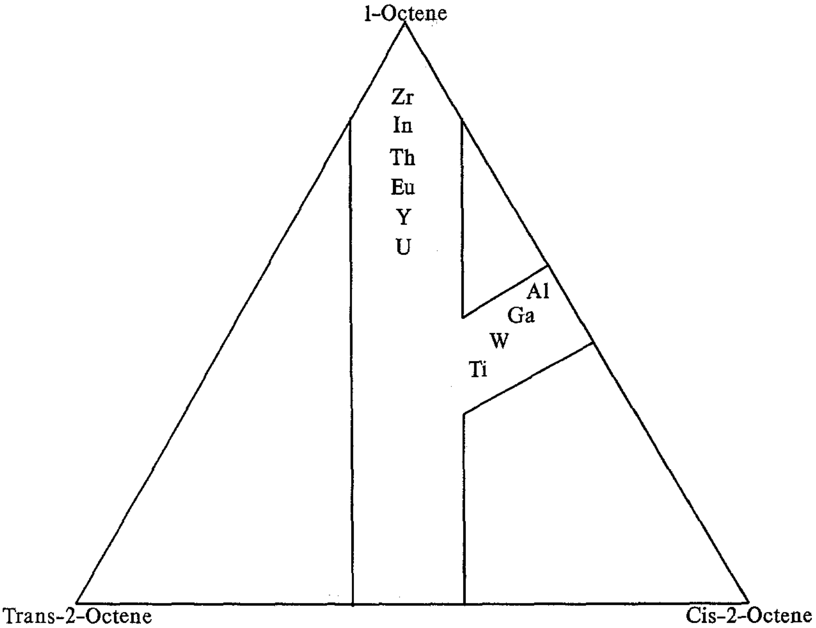


FIG. 7. Schematic of the product selectivities defined by the alkene products from the conversion of 2-octanol with metal oxide catalysts (see text).

the acid–base pair is decreasing in strength. Thus, the coordinatingly unsaturated sites that expose the metal cation to chemisorb alcohol exhibit a selectivity that is determined by steric effects for the smaller cations and by base strength for the larger cations.

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