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Catalytic Conversion of Alcohols

XXI. Comparison of Aluminum and Molybdenum Oxide Catalysts

BURTRON H. DAVIS

Institute for Mining and Minerals Research, University of Kentucky, P. O. Box 13015, Lexington, Kentucky 40512

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Molybdena, as a very selective dehydration catalyst, resembles alumina. Neither catalyst causes isomerization of the initial gas-phase alkene dehydration products. This was confirmed by adding a similar alkene to an alcohol reactant. However, molybdena produced products from some alcohol reactants that even required methyl migrations. For example, dehydration of 4,4-dimethyl-2-pentanol with molybdena produced primarily β-elimination products, whereas the isomeric 2,2-dimethyl-3-pentanol produced only about 10% β-elimination with the remaining dehydration products requiring isomerization by methyl migration. On the basis of alkene distributions from cyclic and acyclic alcohols, molybdena catalyzes dehydration by an E-1-like mechanism in contrast to the concerted mechanism for alumina.

INTRODUCTION

Characterization of the site responsible for catalytic activity is necessary before detailed mechanisms can be written for catalytic reactions. Great strides have been made during the past few years in developing instrumental techniques to examine catalysts and to elucidate features at the molecular level. However, we are still a long way from being able to define sites in heterogeneous catalysts as can be done for many of the homogeneous complexes. This means that indirect methods, particularly studies of organic reactions, will play an important role in defining the catalyst site for years to come.

The conversion of alcohols provides a number of parallel reaction paths and, consequently, a number of product selectivities. Organic chemists have found that elimination from many systems, such as 2-methylcyclohexanol, follows an *anti* elimination pathway (*1*). This steric preference for the elimination mechanism may also determine the elimination product from acyclic alcohols. Bartsch *et al.* (*2*) have observed that the size of the base will influence elimination to favor the *cis* isomer. In addition, it appears that elimination on a surface, such as one finds in heterogeneous catalysts, may impose additional steric requirements.

Davis (*3*) observed that many metal oxides catalyze elimination of water from alcohols to produce about the same amount of the *cis* and *trans*-2-alkene isomers from 2-ols, even though the amount of 1-alkene produced may vary from 30% to greater than 95%. Only a few of the oxides studied—aluminum, gallium, and tungsten oxide—deviated from this pattern. For these few oxides there was a decided preference for the *cis* isomer over the *trans* isomer.

Similar results were observed with 2-methylcyclohexanol isomers. Most catalysts caused *cis*—*trans* isomerization of the reactant as well as dehydrogenation of the alcohol to the corresponding ketone. Only a few catalysts, notably alumina, gallia, and tungsten oxide, exhibited a preference for the *anti* elimination product, 3-methylcyclohexene.

Molybdena is an important catalyst for hydrotreating and for coal liquefaction (*4*). As such, it is widely used in commercial catalysts and is widely studied. Consequently it is of interest to compare the cata-

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lytic character of molybdena to that of other metal oxide catalysts. In this presentation we make a detailed comparison of molybdena to alumina, the usual support for most commercial catalysts. The significant difference between the alkene selectivities obtained with these two catalysts suggests that this may be a means to characterize surface coverage by molybdena oxide; this is currently being investigated. The data for molybdena also permit ranking of this catalyst with respect to a number of Periodic Table neighbors that have been described previously.

TABLE 1

Octene Distribution Obtained from the Dehydration of 2-Octanol with a Molybdena Catalyst at Various Temperatures

Temperature (°C)	LHSV	Conversion (mole%)	Octene (mole%)		
			1-	*trans*-2-	*cis*-2-
203	9.2	10	20	46	34
200	2.8	60	23	39	38
225	11	75	24	37	39
180[a]	0.92	34	22	38	40

[a] Different catalyst batch.

EXPERIMENTAL

The conversions were carried out at 1 atm alcohol pressure without diluent. The catalyst was held in a plug flow reactor and was calcined *in situ*. After a run (four to ten sample collections during 1 to 8 h) the catalyst was regenerated in air. Experimental details were described previously (*5*).

The molybdena catalyst was prepared by precipitation from ca. 1 *M* solution of sodium molybdate by adding hydrochloric acid. The precipitate was washed 12 times with distilled water by repeated filtration–redispersion cycles. The gel was dried in air at 120°C prior to calcination at 400°C in air.

The alumina used in the present study was obtained by precipitation from an aluminum chloride solution by adding ammonium hydroxide (*6*). It was washed with distilled water until chloride was not detected in the wash water by an $AgNO_3$ test. After drying at 120°C, it was calcined in air at 600°C.

Products were analyzed for conversion by gas chromatography (gc) using a Carbowax 20M column. Alkenes were determined using the column (OV-1,β,β′-oxydipropionitrile, or Carbowax 20M) appropriate for the alkene mixture. A diglycerol column operated isothermally at 100°C was used to analyze for *cis*- and *trans*-2-methylcyclohexanol.

RESULTS

The data in Table 1 show that, in the temperature range 180 to 225°C, the alkene distribution does not depend on temperature. The alkene distribution is unique since the amount of *trans*-2-octene is much higher than was obtained with most oxide catalysts. Likewise, the amount of 1-octene is lower than was obtained with most oxides. At all temperatures the molybdena catalyst produced mostly alkenes (greater than 95% dehydration selectivity). The determination of dehydration selectivity is uncertain because the alcohol reactant contained small amounts of the ketone. This requires one to take the difference of two small numbers which makes it difficult to obtain an accurate measure of the amount of dehydrogenation; it is likely that molybdena has a dehydration selectivity greater than 95%.

Secondary isomerization reactions may alter the initial alkene distribution. We have previously used the isomerization of a similar alkene added to the alcohol charge to estimate the extent of secondary isomerization reactions. A mixture of 2-pentanol and 1-octene (18 mole%) was converted over the molybdena catalyst at 180°C using conditions similar to those reported in Table 2. The pentene composition obtained during this run was identical to those in Table 2. However, less than 0.01% of the added 1-octene was isomerized to 2-octene isomers.

TABLE 2

Conversion of Pentanols with a Molybdena Catalyst

Reactant	Conversion (mole%)	Pentene (mole%)		
		1-	*trans*-2-	*cis*-2-
2-Pentanol[a] (180°C)	12	27	35	38
3-Pentanol[a] (180°C)	18	7	48	44
Equilibrium	—	11	60	29

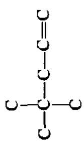
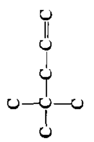
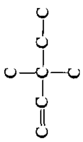
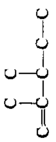
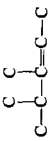
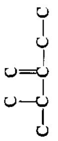
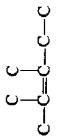
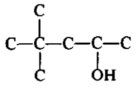
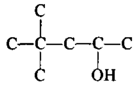
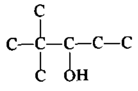
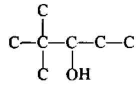
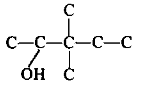
[a] 30 wt% pentanol in 2-octanol; mixture run without dilution.

Thus, the pentenes in Table 2, and presumably the octenes in Table 1, are the primary alkene products desorbing to the gas phase.

Pentanols containing a quaternary carbon (with dimethyl substitution) were dehydrated with alumina and molybdena catalysts (Table 3). With 4,4-dimethyl-2-pentanol, alumina catalyzed dehydration without skeletal isomerization of the alkene products. Apparently the bulk of the neopentyl group on the carbinol carbon provided sufficient steric interaction with the alumina catalyst to produce more of the terminal alkene than was obtained with the unsubstituted 2-pentanol (*8*); likewise, the relative amount of the *trans*-2-isomer was

TABLE 3

Alkene Products from the Dehydration of Secondary Pentanols Containing a Quaternary Carbon Using an Alumina or Molybdena Catalyst

Catalyst	Temperature (°C)	Reactant	Alkene (mole%)[a]								Conversion (mole%)
											
				trans	*cis*						
Mo[b]	180	 $\mathrm{C{-}C(C)_2{-}C{-}CH(OH){-}C}$	36	46	11	—	5.4	—	—	—	25
Al[c]	220	 $\mathrm{C{-}C(C)_2{-}C{-}CH(OH){-}C}$	55	15	30	—	—	—	—	—	35
Mo[b]	180	 $\mathrm{C{-}C(C)_2{-}CH(OH){-}C{-}C}$		1.5	8	—	37	18	—	34	7
Al[b]	180	 $\mathrm{C{-}C(C)_2{-}CH(OH){-}C{-}C}$	21	44	35	—	—	—	—	—	5
Al[d]	275	 $\mathrm{C{-}CH(OH){-}C(C)_2{-}C{-}C}$		—	—	78	5	7.2	7.7	1.4	4

[a] Some percentages may not sum to 100% because of minor products and/or rounding-off percentages.

[b] The pentanol was present at about 10 mole% in 2-octanol; the two alcohols were passed over the catalyst at 1 atm pressure without diluent.

[c] Data from Ref. (*8*).

[d] Data from Ref. (*9*); catalyst was an acidic alumina with 10% piperidine in the alcohol charge.

greater than with the unsubstituted 2-pentanol. With 4,4-dimethyl-2-pentanol, molybdena produced only minor amounts of products from skeletal isomerization. However, the 4,4-dimethyl-1-pentene and 4,4-dimethyl-2-pentene ratio produced by the molybdena catalyst was very different from that of the alumina catalyst. The alkenes from molybdena-catalyzed dehydration of 4,4-dimethyl-2-pentanol resemble those obtained with molybdena-catalyzed dehydration of 2-octanol where a lower amount of the 1-alkene and a greater amount of the *trans*-2-isomer were formed than for alumina-catalyzed dehydration.

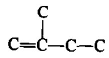
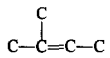
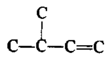
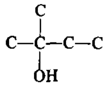
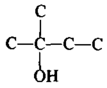
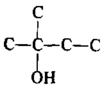
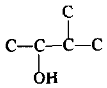
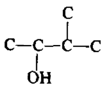
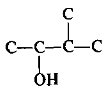
The alkene distribution from 4,4-dimethyl-2-pentanol dehydration differed markedly from those of the alcohol with a hydroxyl group adjacent to a quaternary carbon. With the alumina catalyst, both 2,2-dimethyl-3-pentanol and 3,3-dimethyl-2-pentanol produced little, if any, alkenes which result from skeletal isomerization. The run with 3,3-dimethyl-2-pentanol was at 275°C; the higher temperature probably accounts for the minor amounts of skeletal-isomerization products with this alcohol but not with 2,2-dimethyl-3-pentanol at 180°C. Again, the dehydration products obtained using molybdena differs from those obtained using alumina. About 90% of the alkenes obtained from the molybdena-catalyzed dehydration of 2,2-dimethyl-3-pentanol were those resulting from skeletal isomerization even though the 2,2-dimethyl-3-pentanol was mixed with 2-octanol (86 mole% 2-octanol). Molybdena did not catalyze skeletal isomerization of the alkene products from 4,4-dimethyl-2-pentanol dehydration even though this reactant was not mixed with 2-octanol. Since skeletal-isomerized alkenes were obtained from molybdena-catalyzed dehydration of 2,2-dimethyl-3-pentanol but not from 4,4-dimethyl-2-pentanol, the skeletal isomerization must have resulted during the dehydration step and not as a secondary reaction occuring after alkene desorption to the gas phase.

The pentene distributions from the dehydration of 2-pentanol (Table 2) are similar to those obtained from the conversion of 2-octanol. The pentenes obtained from the dehydration of 3-pentanol show that molybdenum may catalyze some positional isomerization since a small amount of 1-pentene was formed. *trans*-2-Pentene and *cis*-2-pentene were formed in about equal amounts from 3-pentanol. We had earlier shown that secondary isomerization reactions, when using an alumina catalyst, could alter the primary alkene distribution (*7*). However, isomerization did not appear to occur when 2-butanol was converted with alumina with an excess of 2-octanol (*8*) or with the addition of 10 wt% piperidine (*9*). In the present study both 2-pentanol and 3-pentanol were mixed with 2-octanol so that, if molybdena resembles alumina, secondary reactions should have been of minor consequence in determining the alkene distributions using molybdena catalysts. Thus, the 1-pentene from 3-pentanol may be formed from γ-elimination or by a surface isomerization prior to desorption; experimental distinction between these two reaction pathways will be difficult.

Methylbutanols were converted with the molybdena catalyst at 180°C (Table 4). For the conversion of 2-methyl-2-butanol about equal amounts of the two alkenes allowed by β-elimination are obtained. No more than traces of the isomer not allowed by β-elimination, 3-methyl-1-butene, was formed from the dehydration of 2-methyl-2-butanol with either alumina or molybdena catalysts. The products from the dehydration of 3-methyl-2-butanol differ from those from 2-methyl-2-butanol. With 3-methyl-2-butanol a considerable amount of the alkene not allowed by direct β-elimination, 2-methyl-1-butene, was formed; molybdena produced more of this isomer than the alumina catalyst did. More 1-alkene was formed from 2-butanol than from 3-methyl-2-butanol. For 3-methyl-2-butanol less 1-alkene was obtained using the molybdena catalyst than the aluminum catalyst. The

TABLE 4

Products from the Conversion of Methylbutanols with Molybdenum and Aluminum Oxide Catalysts

Catalyst	Temperature (°C)	Reactant	Conversion (mole%)	Alkene (mole%)		
				 $\mathrm{C{=}\overset{C}{C}{-}C{-}C}$	 $\mathrm{C{-}\overset{C}{C}{=}C{-}C}$	 $\mathrm{C{-}\overset{C}{C}{-}C{=}C}$
Mo	180	 $\mathrm{C{-}\underset{OH}{\overset{C}{C}}{-}C{-}C}$	30	45	55	—
Al[a]	220	 $\mathrm{C{-}\underset{OH}{\overset{C}{C}}{-}C{-}C}$	36	50	50	—
Al[b]	275	 $\mathrm{C{-}\underset{OH}{\overset{C}{C}}{-}C{-}C}$	29	58	42	—
Mo	180	 $\mathrm{C{-}\underset{OH}{C}{-}\overset{C}{C}{-}C}$	30	26	67	6.8
Al	220	 $\mathrm{C{-}\underset{OH}{C}{-}\overset{C}{C}{-}C}$	70	9	66	25
Zr	—	 $\mathrm{C{-}\underset{OH}{C}{-}\overset{C}{C}{-}C}$	2.0	0.2	6	94
Equilibrium	180	—		23.0	75.5	1.25

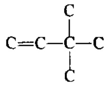
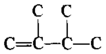
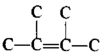
[a] From Ref. (*8*).
[b] From Ref. (*9*).

three methylbutene products from 3-methyl-2-butanol are present in approximately the equilibrium amounts with molybdena but not with alumina.

The dehydration products from 3,3-dimethyl-2-butanol also emphasize the difference in the catalytic properties of alumina and molybdena. With an alumina (Table 5) catalyst 70% or more of the products was 3,3-dimethyl-1-butene, the product from direct β-elimination. The other products from dehydration of this alcohol are those from skeletal isomerization to dimethylbutenes. Greater than 80% of the dimethylbutenes formed using the alumina catalyst is the 2,3-dimethyl-1-butene isomer; this is opposite to that of thermodynamic stability. Furthermore, the methylbutenes formed from the dehydration of 3,3-dimethyl-2-butanol with alumina are the same as those obtained from the dehydration of 2,3-dimethylbutanol with an alumina catalyst (Table 6). Alumina produced a similar alkene distribution over the temperature range 180–340°C for 3,3-dimethyl-2-butanol. A much different alkene composition was obtained from 3,3-dimethyl-2-butanol with a molybdena catalyst. Only 4% of the primary dehydration product, 3,3-dimethyl-1-butene, was obtained; this was the result even when the 3,3-dimethyl-2-butanol was diluted with 2-octanol. Furthermore, the dimethylbutenes obtained using the molybdena catalyst were markedly different from those obtained

TABLE 5

Products from the Dehydration of 3,3-Dimethyl-2-butanol, with Molybdena and Alumina Catalysts

Catalyst	Temperature (°C)	Conversion (mole%)	Alkene (mole%)		
			 $C{=}C{-}\overset{C}{\underset{C}{C}}{-}C$	 $C{=}\overset{C}{C}{-}\overset{C}{C}{-}C$	 $C{-}\overset{C}{C}{=}\overset{C}{C}{-}C$
Mo[a]	180	14	3.5	44	52
Mo[b]	180	18	4.0	44	52
Al[b]	180	14	72	23	4.3
Al[c]	280	83	70.3	25.6	2.8
Al[c]	340	16	78.1	17.3	1.6
Equilibrium	180 327		2.95 4	31.3 44	65.7 52

[a] Pure reactant without diluent.

[b] 25 wt% in 2-octanol.

[c] From Ref. (9); minor amounts of other products were reported so that the total in this table does not add up to 100%.

with an alumina catalyst. In fact, the alkenes obtained using the molybdena catalyst were essentially the equilibrium composition.

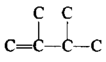
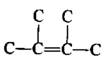
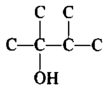
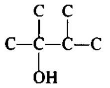
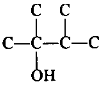
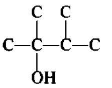
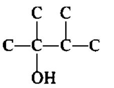
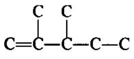
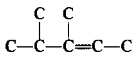
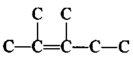
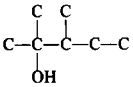
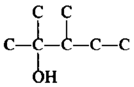
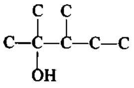
The products from the alumina-catalyzed dehydration of a tertiary alcohol, 2,3-dimethyl-2-butanol (Table 6), are far from the equilibrium composition with the less stable 2,3-dimethyl-1-butene the predominant product. With a molybdena catalyst, the alkene products from this alcohol are much closer to the equilibrium composition. The alkenes from 2,3-dimethyl-2-pentanol dehydration follow the same pattern as those from 2,3-dimethyl-2-butanol.

The alkene distributions obtained from the dehydration of methylpentanols are presented in Table 7. For a tertiary alcohol, 2-methyl-2-pentanol, molybdena produces only slightly less of the terminal alkene, 2-methyl-1-pentene, than alumina does. Both catalysts produce more than the equilibrium amount of the terminal alkene. Only traces of the methylpentenes not allowed by β-elimination are obtained with either catalyst.

With 4-methyl-2-pentanol and an alumina catalyst only traces of pentenes other than the expected 4-methyl-1-pentene and 4-methyl-2-pentene were formed; *cis*- and *trans*-4-methyl-2-pentenes were not separated by the gc columns we used. However, the molybdena catalyst caused isomerization since 2-methyl-1-pentene and 2-methyl-2-pentene were formed in addition to the alkenes expected from 4-methyl-2-pentanol dehydration. In addition, alumina-catalyzed dehydration produced more 4-methyl-1-pentene isomer than did molybdena; however, both catalysts produced about the same amount of terminal alkene (1- vs the 2-alkene) as would be expected based on the alkenes formed by each catalyst for an unsubstituted 2-ol. The products from the dehydration of the third methylpentanol, 2-methyl-3-pentanol, differ from either of the above two alcohols. Both catalysts produced a significant amount of alkenes not allowed by direct β-elimination of water. With the alumina catalyst 8.6% of 2-methyl-1-pentene was produced in addition to the two alkenes allowed by β-elimination. About equal amounts of the two alkenes allowed by β-elimination were

TABLE 6

Alkene Products from the Dehydration of 2,3-Dimethyl Tertiary Alcohols

Catalyst	Temperature (°C)	Alcohol	Conversion (mole%)	Dimethylbutene (mole%)		
				 $\mathrm{C{=}C(C){-}C(C){-}C}$	 $\mathrm{C{-}C(C){=}C(C){-}C}$	
Mo	180	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C}$	38	55	45	
Mo	140 (LHSV = 23)	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C}$	38	51	49	
Mo	140 (LHSV = 90)	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C}$	7	50	50	
Al[a]	275 345	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C}$	18 85	87 89	9 9.7	
Al	220	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C}$	18	84	16	
Equilibrium	180		—	32	68	
				Dimethylpentene (mole%)		
				 $\mathrm{C{=}C(C){-}C(C){-}C{-}C}$	 $\mathrm{C{-}C(C){-}C(C){=}C{-}C}$	 $\mathrm{C{-}C(C){=}C(C){-}C{-}C}$
Mo	180	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C{-}C}$	45	48	15[b]	37
Al	180	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C{-}C}$	70	62	8[b]	30
Al[a]	275	 $\mathrm{C{-}C(C)(OH){-}C(C){-}C{-}C}$	100	92	—	7.9

[a] From Ref. (9).

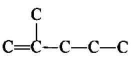
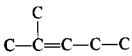
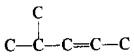
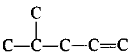
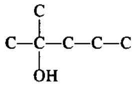
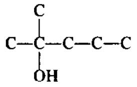
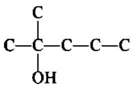
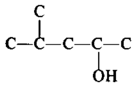
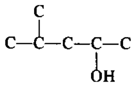
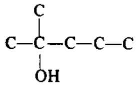
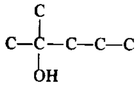
[b] Tentative identification based on gc retention time.

formed, whereas about 4.3 times as much of the 2-methyl-2-pentene would be formed if an equilibrium distribution had been obtained. Molybdena, on the other hand, produced a nearly equilibrium methylpentene composition; only the (4-methyl-2-pentene/2-methyl-2-pentene) ratio was slightly higher than would be present at equilibrium. In the above equilibrium compositions, only the alkenes permitted without a methyl migration are considered.

The data in Table 8 also emphasize the difference between the two catalysts. With 3-methyl-3-pentanol, neither catalyst produced a measurable amount of 3-methyl-1-pentene; however, the equilibrium amount

TABLE 7

Alkene Products from the Dehydration of Methylpentanols

Catalyst	Temperature (°C)	Reactant	Conversion (mole%)	Methylpentene (mole%)			
				 $\mathrm{C{=}\overset{C}{C}{-}C{-}C{-}C}$	 $\mathrm{C{-}\overset{C}{C}{=}C{-}C{-}C}$	 $\mathrm{C{-}\overset{C}{C}{-}C{=}C{-}C}$	 $\mathrm{C{-}\overset{C}{C}{-}C{-}C{=}C}$
Mo	180	 $\mathrm{C{-}\overset{C}{\underset{OH}{C}}{-}C{-}C{-}C}$	60[a]	50	50	tr	tr
Al	165	 $\mathrm{C{-}\overset{C}{\underset{OH}{C}}{-}C{-}C{-}C}$	8.0	70	30	—	—
Al	215	 $\mathrm{C{-}\overset{C}{\underset{OH}{C}}{-}C{-}C{-}C}$	18	70	30	—	—
Mo	180	 $\mathrm{C{-}\overset{C}{C}{-}C{-}\underset{OH}{C}{-}C}$	20	8	4.5	60	26
Al	175	 $\mathrm{C{-}\overset{C}{C}{-}C{-}\underset{OH}{C}{-}C}$	28			53	47
Mo	180	 $\mathrm{C{-}\overset{C}{\underset{OH}{C}}{-}C{-}C{-}C}$	40	23	49	26	2.7
Al	180	 $\mathrm{C{-}\overset{C}{\underset{OH}{C}}{-}C{-}C{-}C}$	15	8.6	44	47	tr
Equilibrium	180			23	62	14	1

[a] 25 wt% 2-methyl-2-pentanol in 2-octanol.

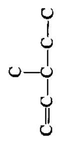
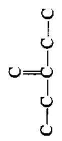
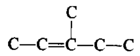
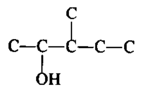
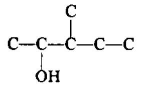
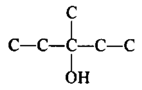
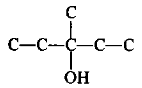
of this isomer is only about 1% so the small amount obtained may not be significant. For the three isomers allowed by β-elimination from 3-methyl-3-pentanol, the two catalysts produce very different distributions. Alumina shows a strong selectivity for the 3-methyl-*cis*-2-pentene over 3-methyl-*trans*-2-pentene; in this respect it shows the well-established *cis* preference for alkene products (*9*). Molybdena, on the other hand, produces an equilibrium *cis*/*trans* ratio for the 3-methyl-2-pentenes; at the same time the amount of the less stable alkene, 2-ethyl-1-butene, is about three times greater than the equilibrium amount.

With 3-methyl-2-pentanol, alumina produces an alkene distribution that is similar to that obtained with 4-methyl-2-pentanol. Molybdena again produces an alkene distribution that, except for the amount of 3-methyl-1-pentene, is an equilibrium composition.

The results from the conversion of 2-methylcyclohexanol isomers with molybdena and alumia are shown in Table 9. The product distributions do not change with time for the molybdena catalyst for either reactant. From the conversion of *cis*-2-methylcyclohexanol, 86% of the dehydration products are the more stable 1-methylcyclohexene, there was very little dehydrogenation, and isomerization of the reac-

TABLE 8

Products from the Conversion of 3-Methylpentanols with Molybdena and Alumina Catalysts

Catalyst	Reactant	Conversion (mole%)	Temperature (°C)	Alkene (mole%)			
						 $\mathrm{C{-}C{=}C(C){-}C{-}C}$	
						trans	*cis*
Mo	 $\mathrm{C{-}C(OH){-}C(C){-}C{-}C}$	16[a]	180	9	9.5	54	27
Al	 $\mathrm{C{-}C(OH){-}C(C){-}C{-}C}$	12[a]	180	25	tr	28	47
Mo	 $\mathrm{C{-}C{-}C(C)(OH){-}C{-}C}$	35	180	—	18	50	32
Al	 $\mathrm{C{-}C{-}C(C)(OH){-}C{-}C}$	18	220	—	18	52	30
Equilibrium			180	1.0	6.7	55.5	36.5

[a] 9% reactant in 2-octanol.

tant to the *trans*-2-methylcyclohexanol isomer was not observed. Molybdena and alumina produce similar products for the conversion of *cis*-2-methylcyclohexanol but this similarity does not apply for the two catalysts with *trans*-2-methylcyclohexanol. Both molybdena and alumina are selective dehydration catalysts which do not isomerize the reactant to the other alcohol isomer for the *trans*-2-methylcyclohexanol reactant. However, about 80% of the less stable 3-methylcyclohexene was obtained using the alumina catalyst whereas only 42% of the 3-methylcyclohexene isomer was obtained when using the molybdena catalyst.

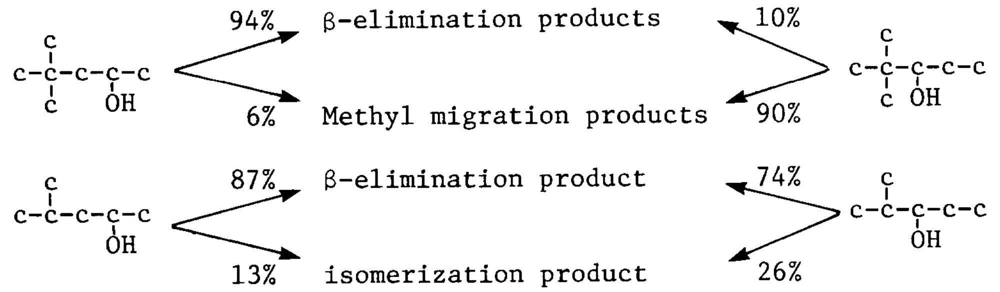
The alkene distributions from the two alcohol isomers do eliminate a common transition state for the methylcyclohexanols with either molybdena or alumina.

DISCUSSION

On a weight basis, and certainly on a surface area basis, molybdena is as, or more, active and selective for the dehydration of secondary and tertiary alcohols than alumina is.

Molybdena undergoes reduction when in contact with a secondary alcohol. The catalyst, from visible observation, is reduced to the blue oxide form as the alcohol wave progresses through the catalyst bed. Even after several hours on stream, the amount of dehydrogenation products is inadequate to provide sufficient hydrogen to reduce an appreciable fraction of the bulk catalyst to $MoO_{2.5}$. Catalyst activity and selectivity do not change during several hours of reaction. Therefore, it appears that, once a reduced surface layer is formed, the catalyst does not undergo further change as far as alcohol conversion and product selectivity are concerned.

A number of alcohol isomers, each possessing a common carbon skeleton, were dehydrated; the fraction of alkene products that were derived from a β-elimination was not the same for all alcohol isomers. For example, the alkenes from 4-methyl-2-pentanol and 2-methyl-2-pentanol are those expected for β-elimination. However, the alkenes from 2-methyl-3-pentanol contain a significant amount of 2-methyl-1-pentene, a product not allowed by β-elimination. The alkenes derived from alumina-, as well as molybdena-, catalyzed dehydration of 2-methyl-3-pentanol contain this unallowed alkene. Similar results were also obtained with the methylbutanol system. This trend is likewise observed with the pentanols containing a quaternary carbon when the hydroxyl group is adjacent to the quaternary carbon. For example, molybdena-catalyzed dehydration of 2,2-dimethyl-3-pentanol produces 90% of alkenes derived from methyl group migration. When the hydroxyl group was not adjacent to the quaternary carbon, little isomerization was observed. Thus, the following scheme applies for the molybdena catalyst:



Results such as those shown above for the methylpentanols have been attributed to a γ-elimination mechanism.

Positional isomerization of gas-phase normal alkene product does not appear to occur when an appreciable partial pressure of alcohol is present. Thus, it appears that the observed alkene distribution is the initial mixture that desorbs from the catalytic site. Likewise, the *cis*-2/*trans*-2-alkene distribution is not the thermodynamic ratio in many cases. The (*cis*-2/*trans*-2) ratio obtained with the molybdena does not change with time. A number of metal oxide catalysts produce a nearly equal amount of *cis*-2- and *trans*-2-alkene from the dehydration of 2-ols even though the amount of 1-alkene formed may vary widely (*3*). Only a few metal oxides, e.g., aluminum, gallium, and tungsten, show decided preference for *cis*-2-alkene formation. Thus, while molybdena is a very selective dehydration catalyst, it does not have the high selectivity for the *cis*-2-isomer that alumina does.

For the conversion of the 2-ols molybdena does not produce a *cis*/*trans* equilib-

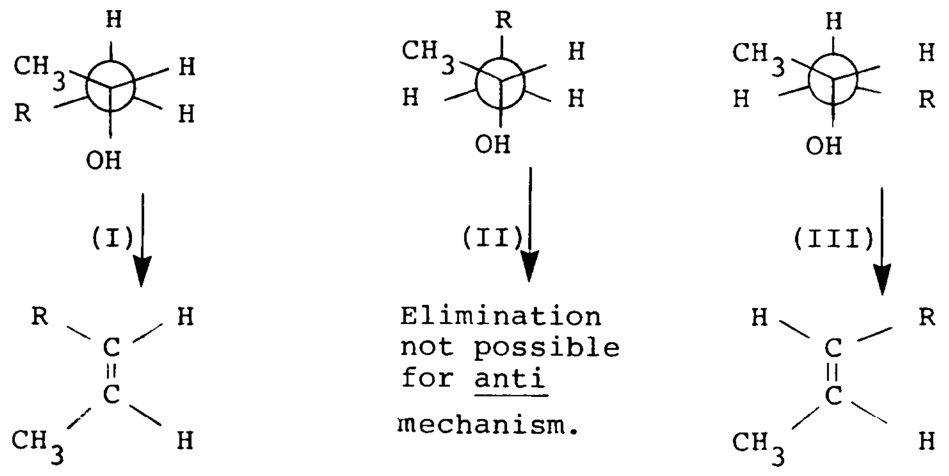
TABLE 9

Products from the Conversion of *cis*- and *trans*-2-Methylcyclohexanol at Atmospheric Pressure

Temperature (°C)	Alcohol	Catalyst	Time (min)	Conversion (mole%)	$\frac{\text{Dehydration}}{\text{Dehydration + Dehydrogenation}}$	$\frac{\text{1-Methylcyclohexene}}{\text{(1-Methylcyclohexene + 2-Methylcyclohexene)}}$	$\frac{\text{Nonreactant methylcyclohexanol}}{\text{Total methylcyclohexanol}}$
180	*cis*	Mo	3	40	0.95	0.85	[a]
			9	36	0.93	0.85	[a]
			23	31	0.93	0.86	[a]
			34	24	0.93	0.86	[a]
			36	24	0.92	0.86	[a]
220	*cis*	Al	—	—	>0.95	0.82	Trace
180	*trans*	Mo	4	33	0.97	0.44	0.023
			10	25	0.97	0.58	0.020
			15	25	0.93	0.58	0.006
			21	24	0.96	0.58	0.004
			26	23	0.96	0.58	0.009
			29	23	0.96	0.58	0.005
220	*trans*	Al	—	—	>0.95	0.20	Trace

[a] *trans*-2-Methylcyclohexanol was not detected (<0.05%).

rium for the 2-alkenes. Rather, nearly equal amounts of *cis*-2-pentene and *trans*-2-pentene, as well as *cis*-2-octene and *trans*-2-octene, were formed. This is what one would expect for an *anti* elimination from the structure shown below if one neglects the interaction between the methyl and R groups.



While much evidence exists to support an *anti* elimination mechanism for cyclic and acyclic alcohols, some data have been interpreted to support the view that elimination over some oxides follows, or partly follows, a *syn* elimination mechanism for the more basic catalysts. A similar alkene distribution could be expected from a *syn* elimination mechanism, perhaps with less of the contribution from structure **I** because of R and CH_3 steric repulsion. However, one could argue that the lower *cis*-alkene yield from structure **I** would be nearly offset because a similar steric hindrance in structure **I** should favor the *cis* isomer over the *trans* isomer in structure (**II**).

The experimental data show that most of the oxides studied, molybdena included, yield about the same amount of the *cis*-2- and *trans*-2-alkene (*3*). However, the amount of 1-alkene varies widely. Following this simplified approach, one could attribute an electronic effect (acidity or basicity) as being responsible for the 1-alkene selectivity within the group of catalysts that produce an equal amount of *cis*- and *trans*-2-alkenes. Following this simple logic one obtains a series, arranged in order of increasing basicity: MoO_3, Al_2O_3, SiO_2, In_2O_3, Nd_2O_3, ZrO_2, ThO_2. This ordering is similar to one obtained when these oxides are arranged on the basis of the reaction with O^{2-} (*10*).

The alkene selectivity then leaves a small group of catalysts which do not follow the above general trend. It appears that a steric consideration of the base, not the reactant, may be responsible for this selectivity. It has been documented by deuterium tracer studies that there is a strong preference for an *anti* elimination pathway over alumina (*11, 12*). Bartsch *et al.* (*2*) have shown that a larger base strongly favors the *cis* isomer. Thus, it appears that for this small group of catalysts the smaller and/or higher-charged cation together with more difficult reducibility, even for the surface layer in some cases, provides a surface with closely packed oxide ions. These oxide ions surrounding the metal ion catalytic site may be viewed collectively as a basic anion. In the case of this group of catalysts the closely packed oxide ions resemble a large basic ion in Bartsch's experiments. Hence, the size of the basic ion needed to abstract the β-H is great enough to more than compensate for the steric effect imparted to the transition state by the reactant in structure **I.** Thus, the steric requirements of the *anti* elimination and the *cis* effect of the large anion could operate so that elimination using this small group of catalysts would be mostly by a transition state resembling structure **I.**

This view may be summarized as follows. There are two groups of catalysts: group A resembles a large basic anion because of the close spacing of the oxide ions due to the smaller, higher-charged cation and/or because of more difficult reduction of even the surface layer and group B has more open, widely separated oxide ions due to the large cations and the more reduced oxide surface, and sometimes even the reduced bulk. With group A catalysts dehydration selectivity will be determined by steric effects imposed on the transition state by the catalyst as well as the reactant. In this, and the following group B discussion, we view dehydration occurring by a concerted mechanism; however, the timing of the sequence may vary so as to resemble, at the extremes, an E-1 or E2cB mechanism. For group A metal oxides, the timing of events is probably such that the base strength plays a very small, if any, role in determining alkene selectivity.

For group B metal oxides, the oxide ions are widely spaced so that elimination resembles that with a small basic ion. For these oxides, base strength will determine the 1-alkene selectivity. For the more acidic metal oxides in group B, the timing of elimination is such that the removal of the β-H occurs late in the concerted mechanism; hence, the stability of the alkene, will be a primary factor in determining the amount of 1- and 2-alkene. However, the more basic metal oxides of group B will follow a different timing sequence so that the transition state will resemble a E2cB mechanism. Here the base will interact with the β-H early in the sequence so that the more acidic methyl hydrogens, rather than the methylene hydrogens, will be abstracted by the small basic oxide ion. Hence, the stronger the small base, the greater the selectivity for the terminal alkene.

REFERENCES

1. Saunders, W. H., Jr. and Cockerill, A. F., "Mechanisms of Elimination Reactions." Wiley, New York, 1973.
2. Bartsch, R. A., Pruss, G. M., Cook, D. M., Buswell, R. L., Bushaw, B. A., and Wiegers, K. E., *J. Amer. Chem. Soc.* **95,** 6745 (1973).
3. Davis, B. H., 7th North American Catalysis Society Meeting, Boston, Mass., October 1981. Paper C-11.
4. Weisser, O., and Landa, S., "Sulfide Catalysts, Their Properties and Applications." Pergamon, New York, 1973.
5. Davis, B. H., *J. Catal.* **52,** 176 (1978).
6. Pines, H., and Haag, W. O., *J. Amer. Chem. Soc.* **82,** 2471 (1960).
7. Davis, B. H., *J. Org. Chem.* **37,** 1240 (1972).
8. Davis, B. H., *J. Catal.* **58,** 493 (1979).
9. Pines, H., and Manassen, J., *in* "Advances in Catalysis and Related Subjects," Vol. 16, p. 49. Academic Press, New York/London, 1966.
10. McGannon, H. E., "The Making, Shaping and Treating of Steel," 9th ed., p. 339. U. S. Steel Corp., Pittsburgh, 1971.
11. Kibby, C. L., Lande, S. S., and Hall, W. K., *J. Amer. Chem. Soc.* **94,** 214 (1972).
12. Blanc, E. J., and Pines, H., *J. Org. Chem.* **33,** 2035 (1968).