

Catalytic Conversion of Alcohols

VI. Selectivity of Indium Oxide

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India, in contrast to two other oxides of group IIIA metals (alumina and gallia), is active for dehydrogenation as well as dehydration. Furthermore, india is selective for the formation of 1-alkenes from 2-ols. Neither the alkene selectivity nor the dehydrogenation-dehydration selectivity changed uniformly as one progressed through the group IIIA metal oxide catalysts. Primary and secondary alcohols reduced indium oxide to an undetermined oxide composition at the reaction temperatures. The dehydrogenation-dehydration selectivity depended on the degree of reduction of the catalyst.

INTRODUCTION

Alumina is a well-known and widely studied catalyst for the dehydration of alcohols (1-3). Two features distinguish the catalytic selectivity of transitional aluminas: (a) a very high selectivity for dehydration and (b) about equal selectivity for the 1- and 2-alkenes from 2-ols but a very much higher *cis*-2-/*trans*-2- ratio than expected on the basis of thermodynamics. Gallium oxide has nearly the same selectivity as aluminum oxide except for a somewhat lower *cis*-2-/*trans*-2- alkene ratio (4).

One of the unifying features of chemistry is the Periodic Table which groups elements with similar chemical properties into families. There are many systematic trends within a given family, e.g., a uniform decrease in electronegativity as atomic number increases. Even though heterogeneous catalysis has been extensively studied for many years and has found application in many commercial processes, no analogous systematization of catalytic

properties exists although some steps have been taken in this direction [for example, see Refs. (5-8)].

One method for classifying catalysts is to study the conversion of a single reactant over a number of catalysts (9). The present work takes a step in this direction by extending the extensive investigations of alumina to another metal oxide of the same family. Few studies have been concerned with alcohol conversion over india and those which have done so are not very extensive (6, 10, 11). Another approach for classifying catalysts is to study the conversion of a number of reactants over a single catalyst. 2-Ols are especially interesting since there are three selectivities: dehydrogenation-dehydration, 1- vs 2-alkene, and *trans*-2- vs *cis*-2-alkene. In the present study, we have examined the conversion of several 2-ols over india as well as two internal secondary alcohols that can only form *cis* or *trans* internal alkenes. A cyclic secondary alcohol and a tertiary alcohol, which can only undergo dehydration, were also included in the study.

EXPERIMENTAL

Catalysts. Indium hydroxide was prepared by precipitation from an aqueous solution of indium nitrate or chloride by adding concentrated ammonium hydroxide to the rapidly stirred solution. The gel was collected and washed by repeated redispersion-filtration cycles. The gel was dried at 120°C and then heated to 550°C in flowing oxygen prior to use. Conditions for the hydrogen pretreatment, if used, are given under Results. After completing a run the catalyst was cooled to room temperature, a flow of air was started, and the catalyst was slowly heated to 250°C. It was held at 250°C for 1-3 hr before increasing the temperature to 500°C and then holding it at this temperature in an oxygen flow for 3 hr.

A sample of indium oxide, after use for alcohol conversion, had a BET surface area of 36 m²/g.

Methods. The alcohol charge was passed over the catalyst at atmospheric pressure without added carrier gas. The alcohol

was charged to a fixed-bed, plug-flow reactor with a syringe pump. Liquid products were collected after passing through a water condenser. The liquid products were analyzed for conversion using temperatures-programmed gas chromatography (gc) with a Carbowax 20 M column. The 2-methylcyclohexanols were analyzed for *cis-trans* composition with a diglycerol column operated at 100°C. Alkenes were analyzed by gc (Ucon, Carbowax 20 M, or β,β' -oxydipropionitrile).

RESULTS

The influence of the pretreatment on the dehydration and dehydrogenation activities is presented in Fig. 1. The dehydration activity of the oxygen-pretreated catalyst increased with time on stream. The oxygen pretreated catalyst was a dull orange color; as the alcohol was passed over the catalyst the color changed to a gray. This indicated that a partial reduction of the catalyst occurred. The orange color could be restored to the used catalyst by heating it in

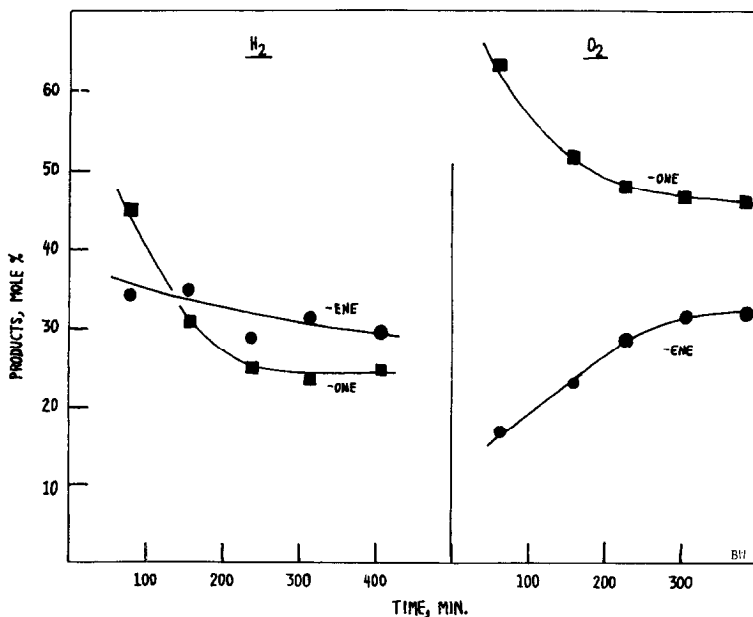


Fig. 1. Influence of hydrogen or oxygen pretreatment on the conversion products from 2-octanol over indium at 250°C for the time period during which the catalyst is exposed to the alcohol.

TABLE 1
Dehydration/Dehydrogenation Selectivity, S , of
Indium Oxide for the Conversion of Alcohols

Alcohol	Temperature (°C)	Pre-treatment atmosphere	S (range)
2-Octanol	215	O ₂	0.45-0.64; 0.14-0.56 ^a
	230	O ₂	1.10-1.12; 0.30-0.62 ^a
	250	O ₂	0.77-0.90; 0.56-0.76 ^a
	255	H ₂	0.68-1.21
2-Pentanol	210	O ₂	0.13-0.22
	235	O ₂	0.18-0.27
	250	O ₂	0.12-0.18
4-Methyl-2-pentanol	225	O ₂	0.22-0.34
	240	O ₂	0.24-0.35
	240	O ₂	0.27-0.29
	260	O ₂	0.17-0.27
	260	O ₂	0.22-0.30
2-hexanol	240	O ₂	0.37-0.45
	237	O ₂	0.33-0.52
Cyclohexanol	235	O ₂	1.87-3.78
	255	O ₂	0.35-0.75
	267	O ₂	0.15-0.27

^a Selectivity range for another run over indium oxide from indium nitrate rather than the india from indium chloride used for all other runs in the table.

flowing oxygen at 95°C. Since indium oxide is reduced to the metal in flowing hydrogen at 500-600°C (12), we are not able to use

the same pretreatment condition as we used with alumina. For the results in Fig. 1 we used a 3-hr pretreatment in flowing hydrogen at 250°C. For the hydrogen-pretreated sample the induction period of increasing dehydration activity was absent; the initial activity was approximately the same as the final dehydration activity of the oxygen-pretreated catalyst. Furthermore, the dehydrogenation activity of the hydrogen-pretreated catalyst was lower than that of the oxygen-pretreated catalyst. These results indicate that catalytic selectivity depends on pretreatment and degree of reduction. Since primary and secondary alcohols themselves are able to reduce the catalyst it was not possible to obtain a true selectivity for the unreduced catalyst. With the tertiary alcohol, 2-methyl-2-butanol, the retention of the yellow-orange color indicated that the catalyst was not reduced, even after 4-6 hr on stream. In fact, the opposite appears to be the case. When a reduced, gray catalyst was used the gray color was gradually replaced by the orange-yellow color. The alkene selectivity pre-

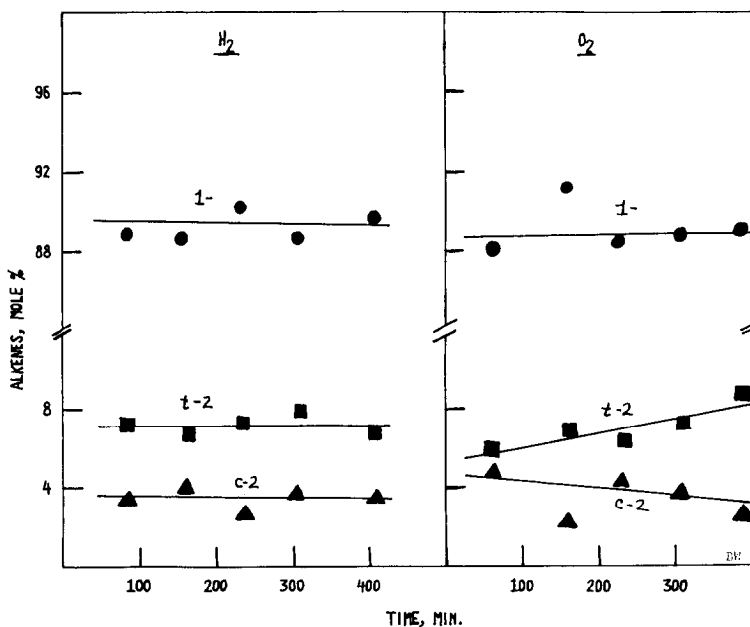


FIG. 2. Comparison of octene isomers from 2-octanol conversion over india pretreated with hydrogen or oxygen (octenes are the same product as shown in Fig. 1).

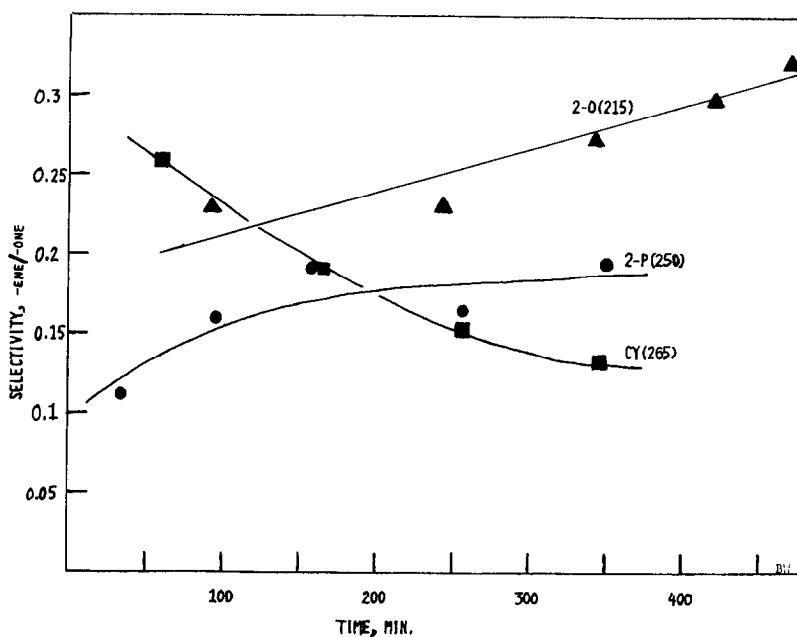


FIG. 3. Representative dehydration-dehydrogenation selectivity changes with time on stream (2-O, 2-octanol; 2-P, 2-pentanol; Cy, cyclohexanol; numbers in parentheses are reaction temperatures).

sented in Fig. 2 corresponds to the runs shown in Fig. 1 and demonstrates that, even though the dehydration-dehydrogenation selectivity changes with time on stream, the alkene selectivity does not. Likewise, the

alkene selectivity did not depend on the pretreatment. The alkene fraction from 2-octanol for both pretreatments contained about 88–90% of the 1-octene isomer. In both cases, more of the *trans*-2- isomer was

TABLE 2

Alkene Distribution from the Conversion of a Mixture of 2-Heptene and 2-Octanol over Indium Oxide

Time on stream (min)	Temperature (°C)	Total conversion (%)	Heptene (mole%) ^a			Octene (mole%)		
			1-	<i>Trans</i> -2-	<i>Cis</i> -2-	1-	<i>Trans</i> -2-	<i>Cis</i> -2-
78	270	97	trace	15.9	84.1	88	10	2.0
140		97	trace	16.1	83.9	85	9.8	5.1
205		96	trace	16.1	83.9	85	9.9	5.7
320 ^b		96	trace	15.9	84.1	86	8.7	5.3
65	270	90	4.9	22.7	72.3	79	15	6.9
126		90	trace	16.1	83.9	87	8.7	4.1
186		81	trace	17.0	83.0	87	8.2	5.0
250		79	trace	16.7	83.3	86	8.2	5.5

^a Charge heptene mixture was 16.1 mole% *trans*-2- and 83.9 mole% *cis*-2- with only traces of the 1-heptene isomer.

^b After this sample was collected, catalyst was treated at room temperature in O₂ and then temperature was increased to 250°C for 1 hr, then to 500°C for 3 hr; cooled to 320°C in O₂ and then treated at 320°C in flowing hydrogen for 3 hr.

TABLE 3
Alkene Distribution from the Conversion of
2-ols over Indium Oxide

Alcohol	Temperature (°C)	Time on stream (min)	Alkene (mole%)		
			1-	<i>Trans</i> -2-	<i>Cis</i> -2-
2-Butanol	210	450	82	8.1	10
	240	425	90	6.1	3.9
	254	195	89	7.0	3.9
2-Pentanol	210	195	67	13	20
	233	510	89	7.9	3.3
	240	370	82	12	5.4
	254	350	89	8.5	2.2
	275	400	61	26	13
2-Hexanol	240	335	89	7.1	4.4
2-Octanol	210	575	93	4.4	2.6
	250	385	89	8.9	2.2
	270	320	86	8.6	5.3
4-Methyl-2- pentanol ^a	202	310	85	15	
	228	420	91	9	
	242	390	92	8	
	258	420	92	8	

^a In addition to the 2-methyl-1- and 2-methyl-2-butene isomers, there were 3-6% of other double-bond positional isomers which have not been included in calculating the reported percentages in this table.

formed than the *cis*-2- isomer. In Table 1 we present the dehydration-dehydrogenation selectivity, *S*, within the limitations of defining a selectivity because of the question of the state of the catalyst reduction. The selectivities represent the range obtained during the run; generally the lower value was obtained at an early time on stream and the higher value of *S* was ob-

tained at a later time on stream. However, cyclohexanol exhibited just the opposite trend for the three temperatures we used in this study. The data in Fig. 3 are representative of the change in *S* with time on stream.

The alkene selectivity from 2-octanol was determined by the surface reaction. The data in Table 2 clearly show that heptene isomers, added to the alcohol reactant, do not undergo isomerization even though the 2-octanol reactant underwent nearly complete conversion to octenes. Furthermore, the octenes obtained at this high conversion had only a slightly lower 1-octene content than was obtained in the low-conversion and lower temperature runs (compare the data in Table 2 with Fig. 2).

In Table 3 we present the alkene composition for the conversion of various 2-ols at several reaction temperatures. Since the alkene distribution does not change significantly during time on stream, only the alkene composition of the final sample collected is given. It is evident that india is very selective in forming the 1-alkene in preference to the 2-alkene. It appears that the selectivity for 1-alkene may decrease at the higher temperatures used (for example, note 2-pentanol at 275°C). At the lowest temperature used, 200-210°C, the selectivity for 1-alkene from 2-butanol,

TABLE 4
Conversion of Internal Hydroxy Alcohols over Indium Oxide

Alcohol	Time on stream (min)	Temperature (°C)	Conversion (mole%)		Alkene (mole%)	
			Dehy- dration	Dehydro- genation	<i>Trans</i> -	<i>Cis</i> -
3-Pentanol	61	238	2.2	56	57 ^a	43
	125	240	2.1	63	69	31
	185	241	1.9	68	71	29
4-Octanol	80	230	12	54	57	43
	190	234	9.3	57	65	35
	247	234	6.8	54	70	30

^a Only traces of the 1-pentene isomer was present for any of the samples.

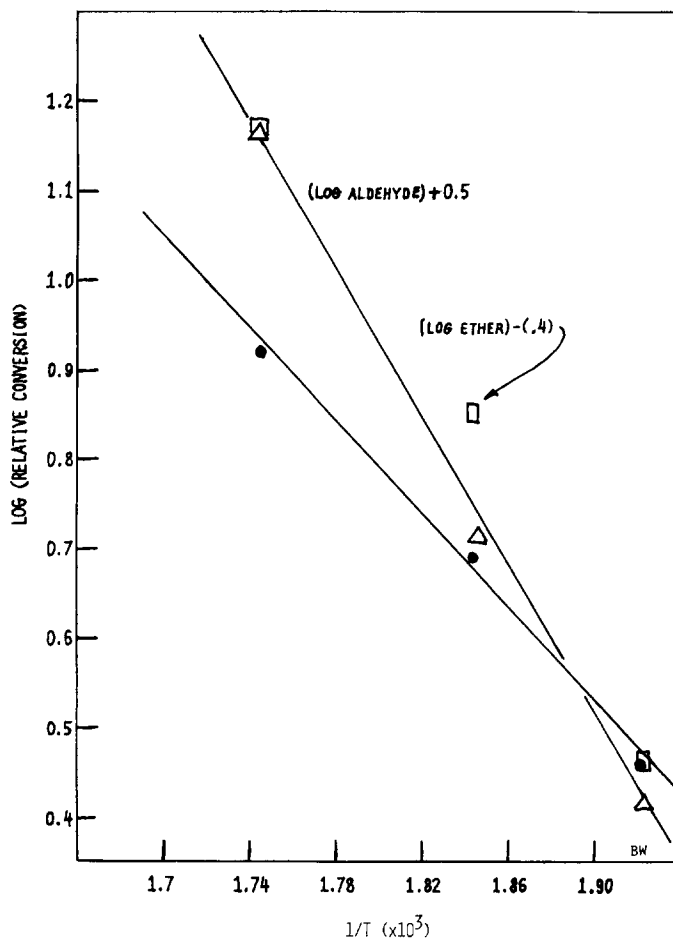


FIG. 4. Arrhenius plot for the conversion of *n*-butanol over indium oxide (○, butenes; △, butyraldehyde; □, di-*n*-butyl ether).

2-pentanol, and 4-methyl-2-pentanol was lower than at the higher temperatures.

3-Pentanol and 4-octanol represented acyclic secondary alcohols that were not capable of forming 1-alkenes as primary reaction products. With 3-pentanol only traces of 1-pentene were obtained so that positional isomerization of the double bond did not occur (Table 4). For the 2-pentene product the *trans* isomer was the dominant product. The data in Table 2 indicate that *cis-trans* isomerization of 2-heptene did not occur; presumably the same would apply for 2-pentene. Consequently it appears that the *cis-2/trans-2-* ratio is approximately 30/70 for the 2-pentenes

from 3-pentanol. We were only able to analyze the octenes for *cis* and *trans* isomers and could not distinguish between *cis-3-* and *cis-4-* or *trans-3-* and *trans-4-* octene. With 4-octanol the *cis/trans* ratio was about 30/70, the same as for 3-pentanol.

The catalyst is not selective for the formation of a 1-alkene from the tertiary 2-ol, 2-methyl-2-butanol. There was a slight increase in the amount of 1-alkene formed as the temperature increased and the amount of 1-alkene was in agreement with that found for other catalysts and for the pyrolysis of the acetate ester (13). The hydrogen- and oxygen-pretreated sample

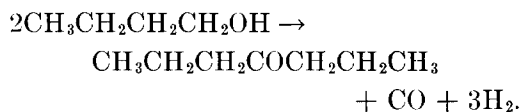
TABLE 5

Alkene Products from the Dehydration of 2-Octanol over Group IIIA Metal Oxide Catalysts

Catalyst	Octene (mole%)		
	1-	<i>Trans</i> -2-	<i>Cis</i> -2-
Acidic alumina	40-45	5-10	50
Nonacidic alumina	30-40	10-25	45-50
Gallia	30	20	50
India	90	8	2

gave approximately 35% of the 1-methyl-1-butene isomer at 185°C and 39% of this isomer at 240°C.

The products from the conversion of the primary alcohol consisted of the dehydrogenation product butyraldehyde, the dehydration product butene, and a third product tentatively identified as di-*n*-butyl ether (Fig. 4). However, the third product could be the condensation product from the reaction



We made the identification as an ether because of a shorter retention time on a Carbowax 20 M column than we would expect for a ketone. The condensation of primary alcohols over dual functional (dehydration and dehydrogenation) catalysts is rather common (14) and we have even observed this condensation with secondary alcohols (15). The temperature coefficients for the conversion of 1-butanol are 12 (butene formation) and 19 kcal/mole (for butyraldehyde as well as for ether formation). In all calculations of the temperature coefficient, a zero-order reaction was assumed; we only verified this assumption experimentally for 2-octanol at 0.5 and 1.0 atm of alcohol pressure. The catalytic activity for the formation of all three products from *n*-butanol was essentially constant during a 500-min run.

The temperature coefficient will depend on the selectivity, *S*, which in turn is dependent on the degree of reduction, and, hence, is subject to considerable error even using the same catalyst batch in the same laboratory. The temperature coefficient was measured with four different samples of indium oxide using the conversion data for 2-octanol for later times on stream. Within the uncertainties given above, the coefficient for 2-octanol was the same for both dehydrogenation and dehydration and was in the range of 27-34 kcal/mole.

DISCUSSION

Indium oxide is a dehydrogenation as well as a dehydration catalyst. Gallia is primarily a dehydration catalyst, and hydrogen-pretreated alumina is primarily a dehydration catalyst. Oxygen-treated alumina can be both a dehydration and dehydrogenation catalyst (15). Gallia was selective for dehydration even when an oxygen pretreatment was used. Thus, the dehydrogenation-dehydration selectivity does not appear to follow a uniform trend but makes an abrupt change in going from gallium oxide to indium oxide. Unfortunately, the three oxides do not have the same crystal structure: γ -alumina is cubic (16), gallia is rhombic, and india is trigonal (17). There is always a question about making comparisons of catalysts with different crystal structures. The ionic radius for the 3+ ion varies uniformly from Al³⁺ to In³⁺ (17); hence, an abrupt selectivity change must be attributed to some effect other than, or in addition to, ionic radius.

The increase in dehydration selectivity for alumina and thoria in going from an oxygen pretreatment to a hydrogen pretreatment was attributed to an increased exposure of the metal ion (18). From the size of the metal ion, we would expect the exposure of the metal ion in the oxide to increase according to Al³⁺ < Ga³⁺ < In³⁺ and would, on the basis of ion exposure, expect the dehydration selectivity to in-

crease in the same order. This expectation was not borne out by the experimental results.

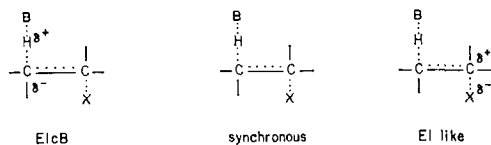
As can be seen in Table 5, the alkene selectivity also underwent an abrupt change between gallia and india. Alumina and gallia, except for a slight difference in the ratio of the 1- and *trans*-2- alkenes, were indistinguishable. On the other hand, india was a very selective catalyst for the formation of 1-alkene and, for the small amount of 2-alkene, gave a much lower *cis*-2-/ *trans*-2-ratio than did the other two catalysts.

In the temperature range used in this study, strong acid heterogeneous catalysts such as silica-alumina yield equilibrium, or near equilibrium, mixtures of alkenes with the same carbon skeleton (19). It is widely accepted that carbonium ions are formed on silica-alumina catalysts (20). Since we did not observe either positional or *cis/trans* isomerization with india, even though 90–95% of the alkene products are the less stable thermodynamic isomers, we do not believe a carbonium ion intermediate is involved in the alcohol dehydration reaction with india.

The same temperature coefficient for dehydration and dehydrogenation would be consistent with a common intermediate. Due to questions concerning the state of india reduction and the dependence of selectivity on the reduction, the temperature coefficients will be subject to question. With 2-pentanol and 2-octanol we obtained the same temperature coefficient for both dehydrogenation and dehydration when we used rate data for the later time on stream. However, our results with 4-methyl-2-pentanol and cyclohexanol cause us to view the 2-pentanol and 2-octanol temperature coefficients with caution.

It is well established that the concerted β -elimination reaction through an *anti*-transition state covers a whole spectrum of mechanisms from the carbanionic E1cB to the carbonium ion-like E1 structure (21). The specific mechanism will depend on the

nature of the reactants and the reaction conditions.



It has also been recognized that the base could fulfill two functions: In addition to attacking the hydrogen on C^{β} -H (E2H) it could accelerate the reaction by nucleophilically assisting C^{α} -X bond fission by a simultaneous attack by the base on the C^{α} atom and the β -hydrogen (E2C).



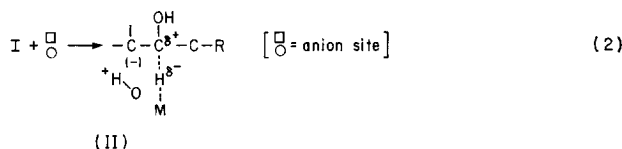
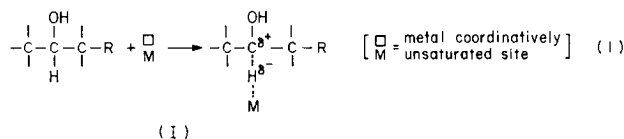
In the liquid phase Bartsch (22) observed that the 1-/2-alkene ratio from the elimination from acyclic 2-alkyl halides and tosylates depended on the strength and size of the base. A change from a dissociated base to a bulky association of several base molecules would increase the proportion of 1-alkene as well as the *cis*-2-/ *trans*-2-alkene ratio. Also, an increase in base strength would favor the 1-alkene isomer.

Eliminations from alcohols and alkyl halides have been interpreted by the above mechanism (2, 23–25). However, india is as active, or more active, for the dehydrogenation of alcohols as for their dehydration. We have at least three possibilities to account for the selectivity over india: (a) The two reactions occur on different sites, (b) a common intermediate is involved in both reactions, or (c) the alcohol can be adsorbed two or more different ways on the same site. The different site concept for alcohol conversion was advanced as early as 1949 by Schwab and Agallidis (26). Earlier, Eucken and Heuer (27) and Wicke (28) had advanced the idea that the

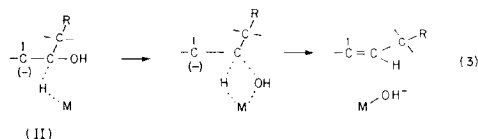
selectivity for ZnO depended on the position of the zinc and oxygen ions. Hauffe (29) advanced the idea that, for a 2-propanol conversion over ZnO, the initial alcohol adsorption began through a hydrogen atom; the selectivity was determined by an initial adsorption of the C^α-H for dehydrogenation and of C^β-H for dehydration.

Since dehydrogenation to a ketone was equal to or exceeded the dehydration reaction to form alkenes with india, the catalyst must be active for C-H bond

scission. This, together with a high selectivity for 1-alkene formation, suggests that a C-H bond scission involving the β-methyl group in the 2-ols may play a role in the selectivity-determining step(s). As with the Hauffe proposal, the alcohol would be adsorbed by a hydrogen atom. In this case the C^α-H would be adsorbed on the metal ion and concurrently, or later, the C^β-H would be adsorbed on an oxygen ion. For clarity we write the adsorption in steps although we would visualize the actual mechanism as a concerted mechanism:

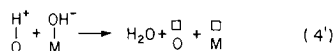
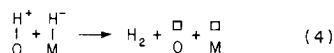


Note that a complete formation of an M-H bond would make the organic portion of structure I a protonated ketone. Protonation of a ketone greatly activates the C^β-H as a proton. The organic portion of structure II, in the limit where the C^α-H bond is completely broken, is just the enol form of a ketone. The ketone forms readily from the enol form and, for most ketones, the equilibrium for the reaction (enol ⇌ ketone) greatly favors the keto form over the enol form. Consequently intermediate II can lead to the dehydrogenation product. Likewise, the following steps lead to the dehydration product from intermediate II.



Examination of models shows that the conformation of the 2-ols is such that large

individual atomic displacements would not be required in the formation of the dehydration or dehydrogenation product. The final step in the mechanism for dehydration and dehydrogenation would be (4) or (4').



While intermediates I and II are well founded in organic chemistry, the overall mechanism is very speculative. However, it does address the need to activate the C-H bonds. As reminded by a referee, the conversion of tertiary alcohols (where a methyl group is substituted for the -H) is more rapid than with secondary alcohols. This appears to be general and we find this to be the case for catalysts which are very selective for dehydration (alumina, gallia), active for both reactions (ThO₂, In₂O₃), and even for those that are very selective

dehydrogenation catalysts (SnO_2). Preliminary results for the competitive conversion of secondary-tertiary alcohol mixtures suggest that even in the mixture the tertiary alcohol undergoes conversion more rapidly. Obviously, the mechanism that we outlined in the Discussion cannot account for the conversion of tertiary alcohols.

Eischens *et al.* (30) first reported ir bands for hydrogen adsorption on ZnO which indicated the adsorption of a hydride ion on the metal Zn^{2+} ion. Knowledge of this adsorption site was expanded by Kokes and co-workers (31) who showed that the sites on ZnO occupied only 5-10% of the surface and that they consisted of isolated metal oxide pairs. Kokes (32) also concluded that "catalysis by zinc oxide resembles, to some degree, homogeneous base catalysis." Support for the formation of a carbanion-like intermediate also comes from a recent ir study which showed that $\text{CD}_3\text{CDODCD}_3$ underwent exchange with the H of a ThO_2 catalyst to form $\text{CD}_2\text{HCDODCD}_3$, etc.

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