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Catalytic Conversion of Alcohols

VII. Alkene Selectivity of Tungsten Oxides

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In agreement with previous reports, tungsten oxides were found to be selective dehydration catalysts. Pretreatment in hydrogen or oxygen did not alter the dehydration selectivity but did alter the alkene distribution. A high *cis*-2/*trans*-2-alkene ratio was obtained from 2-ols with the oxygen-pretreated catalyst; in this respect it resembled alumina. Adding a similar alkene to the alcohol charge showed that the dehydration products were primary ones even in the case of the hydrogen-pretreated sample, which produced a large amount of the *trans*-2-alkene from 2-ols. *Cis–trans* isomerization of 2-methylcyclohexanol did not occur; either the *trans* elimination pathway was not the dominant one with this alcohol or an isomerization of the alkene product occurred prior to desorption.

INTRODUCTION

Sabatier (*1*) summarized the early work on the conversion of alcohols over many oxides. Because of analytical limitations much of the early work was restricted to lower weight alcohols, such as ethanol and propanol, where the only selectivity was the ratio of dehydration to dehydrogenation. Sabatier reported that tungsten oxide was readily reduced by alcohol vapors above 250°C and approached $WO_{2.5}$. This material was reported as an excellent dehydration catalyst for alcohols. In the intervening years tungsten oxide has been widely used as a dehydration catalyst and is now one of the two catalysts recommended by a catalyst manufacturer for this purpose (*2*). Alumina, the other catalyst recommended, has been widely studied and the alkene selectivity has been well documented. In this communication we define some of the alkene selectivities for tungsten oxide.

EXPERIMENTAL

Catalysts. Hydrous tungsten oxide was prepared by adding concentrated hydrochloric acid to an ammonium tungstate solution (ca. 0.5 *M*). The gel was washed 10 times with water by repeated dispersion–filtration cycles. The gel was dried at 120°C in air and pretreated *in situ* at 525 to 550°C.

Experimental. The plug flow reactor and the analytical procedures for the conversion and alkene distribution have been described previously (*3*). All runs were at atmospheric pressure without added carrier gas. After each run the catalyst was cooled to room temperature. Air was passed over the catalyst as the temperature was increased to 100, 250, and 550°C with the sample being held at each temperature for about

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TABLE 1

Dehydration–Dehydrogenation Selectivity for the Conversion of Alcohols over Tungsten Oxide Catalysts

Alcohol	Pretreatment	Temperature (°C)	Selectivity
			-ene/-one
2-Pentanol	O_2	215	7–9
	O_2	245	13–60
3-Pentanol	O_2	255	15–20
2-Hexanol	O_2	265	40–80
4-Methyl-2-pentanol	O_2	235	10–18
	O_2	270	100–200
	O_2	290	60–60
2-Octanol	H_2, H_2O	212	80–100
	O_2	185	150–200
	O_2	240	36–100
	O_2	275	50–75
	O_2	300	35–100
Cyclohexanol	H_2	175	20–80
	H_2, H_2O	178	80–120
	O_2	268	40–90
	O_2	290	80–100
	O_2	308	100–150
trans-2-Methylcyclohexanol	H_2	195	100
	O_2	260	100–150
cis-2-Methylcyclohexanol	O_2	252	50–60
(*cis* + *trans*)-2-Methylcyclohexanol	H_2, H_2O	180	100–130
	H_2, H_2O	195	150–200
	O_2	260	40–100
	O_2	275	100–250

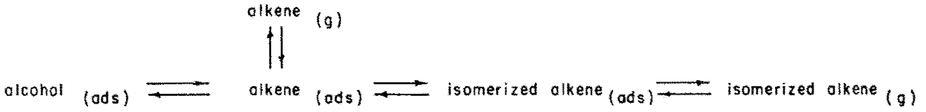
1 hr before increasing to the next temperature. The hydrogen pretreatment, if used, was carried out on the air-treated sample by passing hydrogen over the catalyst at 500°C for 4 hr. In a few pretreatments, the hydrogen was passed through a water bubbler which was at room temperature; the water bubbler was bypassed before decreasing the temperature in the hydrogen flow.

RESULTS AND DISCUSSION

It has long been known that the blue oxide of tungsten is a selective dehydration catalyst for ethanol (*1*). The data in Table 1 show that tungsten oxide is a selective dehydration catalyst for a variety of alcohols. Since the dehydrogenation product was present in very small amounts, the accuracy of the ketone determination introduces a large variation in the selectivity reported in Table 1. Thus, our selectivities should be viewed as showing a general dehydration character rather than an absolute, accurate measure of the selectivity.

Tungsten oxide can be reduced to lower oxides by hydrogen at elevated temperatures. The reduction has recently been studied as an example of the migration of hydrogen from a metal catalyst site to the support and of the influence of hydrogen carrier molecules such as water, alcohols, etc. (*4*). Sabatier (*1*) reported that WO_3 was reduced to a blue oxide with an approximate formula of $WO_{2.5}$; this blue oxide underwent spontaneous reoxidation in air at room temperature. We found that the hydrogen-reduced tungsten oxide catalyst was more active for alcohol dehydration than the oxygen-pretreated sample. The oxygen-pretreated tungsten oxide sample was reduced during the reaction so that, in some cases, the catalytic activity increased with time during the early stages of the reaction before declining due to poisoning (Fig. 1).

The data in Fig. 2 show that the alkene distribution from 2-octanol is quite different for oxygen- and hydrogen-pretreated tungsten oxide catalysts. Over a hydrogen-pretreated catalyst, *trans*-2-octene was the major product (ca. 45%) while over the oxygen-pretreated catalyst it was much lower (ca. 15–20%). The difference in the two catalysts was not due to an isomerization of the type:



If this isomerization scheme operated, the (*cis* + *trans*)-2-heptene that we added to the 2-octanol would have undergone isomerization. The data in Table 2 show that neither positional nor *cis–trans*-2-heptene isomerization occurred. This means that: (a) *trans*-2-octene is formed in a much higher amount over the hydrogen-pretreated tungsten oxide as a primary product, (b) the initial alkene is isomerized before desorbing from the reactive site, or (c) the initial alkene migrates on the surface and isomerizes prior to desorption. An isomerization during the initial adsorption and product formation (b above) should probably be classified as a special

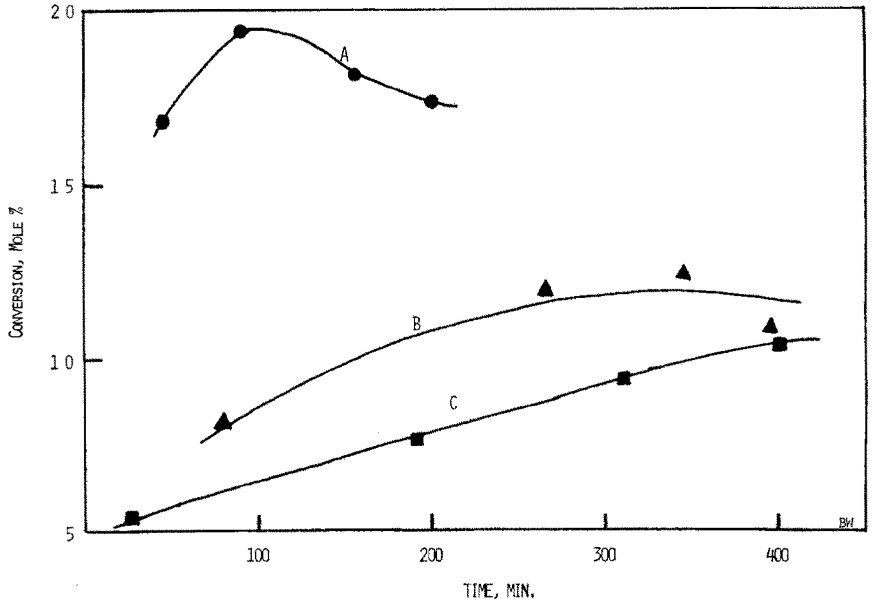


Fig. 1. Representative time dependence of the conversion for some runs over tungsten oxide which showed increasing activity with increasing time (A) 4-Methyl-2-pentanol at 235°C; (B) 2-pentanol at 215°C; (c) 2-pentanol at 245°C; conversion plotted is ⅕th the experimental conversion.

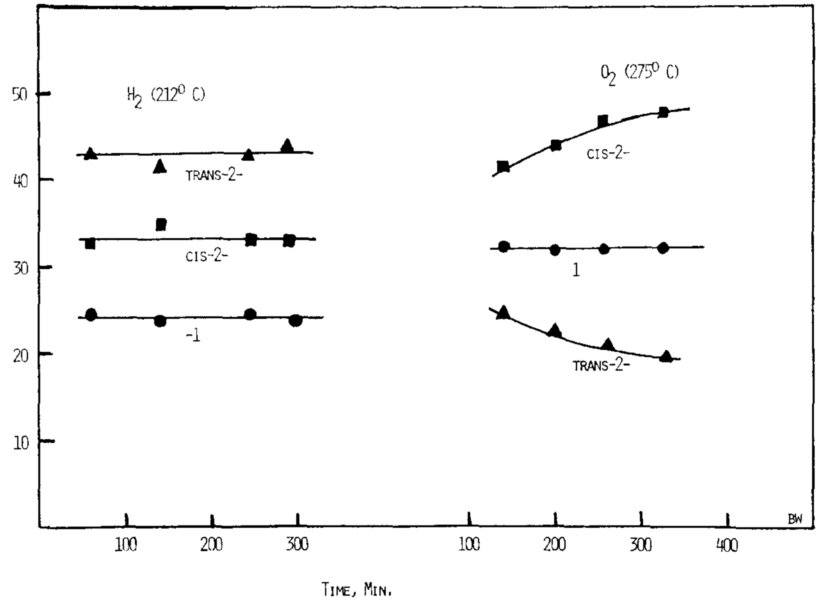


FIG. 2. Alkene distribution from 2-octanol over oxygen and hydrogen pretreated tungsten oxide samples.

feature of scheme a above. Wei has designated scheme c above as disguised kinetics (*5*) and it would be very difficult to demonstrate experimentally. In any event, the alkene distribution that we observe in the gas phase is the distribution of the initial gas phase alkenes.

Table 3 contains alkene selectivities for the conversion of several 2-ols. The conversion of 2-ols are of interest because they provide two selectivities: positional isomers (1- vs 2-alkene) and a *cis–trans* selectivity (*cis*-2-/*trans*-2-alkene). The results with 2-hexanol indicate that the alkene distribution is nearly the same at a high reactant flow rate (8–10% conversion) as it is for a slower flow (45–50% conversion); at most, there is a slight decrease in the *trans*-2-isomer (1–2%) and an increase in the amount of the *cis*-2-isomer (1–2%). Since it was believed that a gas phase alkene product isomerization was eliminated by the results with the addition of 2-heptenes, we would not expect the alkene distribution to change with flow rate changes. The results with 2-pentanol and 2-octanol

TABLE 2

Conversion of a Heptene–2-Octanol Mixture over Tungsten Oxides

Pretreat	Temperature (°C)	Conversion (mol%)	Time (min)	Heptenes (mol%)[a]		Octenes (mol%)		
				cis-2-	*trans*-2-	1-	*trans*-2-	*cis*-2-
H_2	220	18	245	16.7	83.3	21	46	33
		22	252	15.4	84.6	20	46	34
O_2	184	2	184	16	84	32	16	52
O_2	240	7	225	15.4	84.6	32	18	50
		9	305	17.3	82.7	31	17	52

[a] Heptanes in the change were 16% *cis*-2- and 84% *trans*-2-heptane.

TABLE 3

Alkene Distribution from the Conversion of 2-ols over Tungsten Oxides

Alcohol	Temperature (°C)	Time (min)	Conversion (mol%)	Alkenes (mol%)		
				1-	*trans*-2-	*cis*-2-
2-Pentanol[a]	214	180	10	22	20	58
		345	13	26	16	58
		355	11	23	17	60
	245	25	27	22	25	53
		190	38	24	27	49
		310	48	22	33	45
		400	53	19	39	43
2-Hexanol[a]	265	165	47	26	28	46
		240	49	27	26	47
		260	9[b]	28	25	47
		262	8[b]	28	24	48
4-Methyl-2-pentanol[a]	235	155	18	33	66[c]	
		200	18	32	67[c]	
	270	190	35	32	65[c]	
		275	40	32	65[c]	
	290	105	32	29	67[c]	
		120	30	30	66[c]	
2-Octanol[a]	184	184	2	32	16	52
	240	225	7	32	18	50
		305	9	31	17	52
	275	245	25	32	21	47
		315	26	31	20	49
	300	210	35	32	23	45
		235	23	32	25	47
2-Octanol[d]	214	445	46	24	42	34
		530	42	23	44	33
	185	245	10	18	48	34
		330	13	15	47	35
	220	245	18	21	46	33
		252	22	20	46	34

[a] Oxygen pretreatment at 525°C.

[b] Flow rate increased.

[c] Percentage of *cis*-2- + *trans*-2-isomers.

[d] Hydrogen pretreatment except the 185°C run had a hydrogen plus water pretreatment.

suggest that the alkene distribution is temperature dependent; as the temperature increased the amount of 1- and *cis*-2-alkene decreased slightly and the amount of the *trans*-2-isomer increased slightly. It also appears that the amount of 1-alkene increased as the 2-ol chain length increased in going from 2-pentanol to 2-octanol. The amount of the *trans*-2-isomer did not change appreciably so that the increase in the 1-alkene resulted in a corresponding decrease in the *cis*-2-alkene.

The alkenes from 3-pentanol (Table 4) show a high *cis*-2-/*trans*-2-ratio. This ratio is similar to that obtained with gallium oxide but is lower than the 3:1 to 4:1 ratio that have been observed with alumina catalysts. Initially the catalyst did not cause isomerization but as the catalyst was reduced during the run it did become slightly active for positional isomerization of the pentene products.

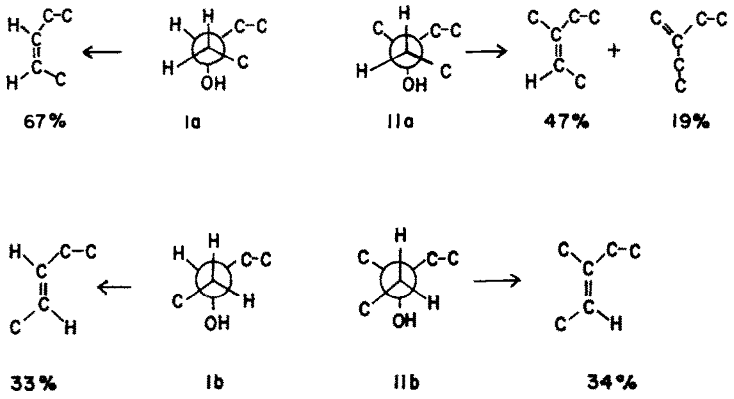
The alkene distribution from the conversion of the tertiary alcohol 2-methyl-

TABLE 4

Results from the Conversion of 3-Pentanol over Tungsten Oxide (Oxygen Pretreatment)

Temperature	Time (min)	Conversion (mol%)	Pentenes (mol%)		
			1-	*trans*-2-	*cis*-2-
250	75	10	—	33	67
	140	8	2.7	34	63
	185	8	3.1	36	61

2-pentanol (Table 5) were in line with those obtained with a wide range of catalysts (*6*). The other tertiary alcohol represented in Table 5, 3-methyl-3-pentanol may be viewed as either a 2-butanol or 3-pentanol substituted at the carbinol carbon. Compared to 3-pentanol, we note the amount of the *trans*-2-isomer from 3-methyl-3-pentanol is the same as from 3-pentanol; this suggests that both 1- and *cis*-2-alkenes may arise from the same pathway in the alkyl substituted reactant that led to *cis*-2-alkene in the unsubstituted 3-pentanol (Scheme 1).



SCHEME 1

It appears that the ethyl–methyl interaction in conformation **IIa** is sufficient to place the carbinol methyl in close proximity to the surface and this leads to the 1-alkene isomer. Viewed as a substituted 2-ol, we would expect an alkene distribution that was similar to 2-pentanol. In making this comparison, we note a similar amount of

TABLE 5

Alkene Composition from the Conversion of Tertiary Alcohols over Oxygen-Pretreated Tungsten Oxides

Alcohol	Temperature (°C)	Time (min)	Conversion (mol%)	Alkene (mol%)			
				1-	*trans*-2-		*cis*-2-
3-Methyl-3-pentanol	180	160	26	19	34		47
		230	22	19	36		45
		315	20	19	33		48
2-Methyl-2-butanol[a]	205	220	45	44		56	
		320	45	45		55	
		460	38	47		53	
		555	33	47		53	

[a] Alkenes are 2-methyl-1-butene and 2-methyl-2-butanol (*cis–trans* isomers not possible).

1-alkene from both alcohols and the formation from the substituted alcohol of a larger amount of the *trans*-2-isomer at the expense of the *cis*-2-isomer. This suggests that the ethyl group provides an interaction in the transition state which favors the formation of the *trans*-2-isomer over the *cis*-2-isomer.

It is apparent from the data in Table 6 that the *cis*-2- or *trans*-2-methylcyclohexanol charge did not undergo a *cis–trans* isomerization when passed over an oxygen-pretreated tungsten oxide catalyst and *trans*-2-methylcyclohexanol did not isomerize over the hydrogen-pretreated catalyst. For example, with the *trans* isomer over the oxygen-pretreated catalyst a minimum of 300 molecules of alcohol underwent conversion to alkenes for each one that underwent a *cis–trans* alcohol isomerization and desorption to the gas phase. The methylcyclohexene composition from *cis*-methylcyclohexanol was about 13% of the 3-methyl isomer and 87% of the 1-methyl isomer; this value has been obtained in the same temperature range with some other isomerizing catalysts so that this appears to be the equilibrium methylcyclohexene composition of these two isomers (*6*). A similar methylcyclohexene composition of about 35% 3-methyl- and 65% 1-methylcyclohexene was obtained from *trans*-2-methylcyclohexanol with both the hydrogen- and oxygen-pretreated catalyst. Thus, tungsten oxide has a much lower selectivity for the 3-methyl isomer from the *trans*-alcohol than an alumina catalyst where the 3-isomer comprises 75 to 80% of the total alkene fraction. Since neither the *cis*- nor the *trans*-2-methylcyclohexanol underwent *cis–trans* isomerization when passed over tungsten oxide, it would appear that a *cis–trans* isomerization would not occur with the mixture. However, if we assume the same alkene selectivity for the *cis*- and *trans*-alcohol for both the pure compound and for the mixture, we calculate that the *cis*-alcohol can only contribute 42% of the total conversion. On the other hand, the analysis of the alcohol fraction from the conversion of the *cis–trans* mixture requires that the *cis*-alcohol account for 77% of the total conversion. Thus, it appears that the reaction of the mixture deviates from the selectivity based on the pure compounds and for the mixture: (a) there is some *cis–trans* alcohol isomerization, (b) there is an isomerization of the alkene fraction to form the less stable isomer, or (c) the alkene selectivity is different.

The temperature coefficients obtained for four of the alcohols (Table 7) are in line with those obtained with other dehydration or dehydrogenation catalysts.

TABLE 6

Conversion of *cis*-2-, *trans*-2-, and (*cis* + *trans*)-2-methylcyclohexanol over Tungsten Oxide

Alcohol isomer	Temperature (°C)	Pretreat	Time (min)	Conversion (mol%)	Alcohol (mol%)		Methylcyclohexene (mol%)			
					cis-	*trans*-	4-	3-	1-	Methylene
trans	195	H_2, H_2O	68	11	0.01	—	0.4	36	60	3.7
trans	261	O_2	60	37	0.1	—	0.8	37	63	—
			120	27	0.1	—	1.3	32	64	2.3
			145	29	0.1	—	0.8	33	61	4.8
cis	252	O_2	90	40	—	0.01	0.6	17	82	0.4
			140	38	—	0.01	—	13	86	0.6
cis + *trans*[a]	260	O_2	245	31	42	58	—	28	72	—
			320	27	46	54	—	28	72	—
cis + *trans*[a]	275	O_2	180	25	49	51	—	25	75	—
			195	25	47	53	—	24	76	—
cis + *trans*[a]	298	O_2	51	47	45	55	—	27	73	—
			66	53	45	55	—	28	72	—

[a] Alcohol mixture contained 53.1% *cis*-2- and 46.9% *trans*-2- alcohol.

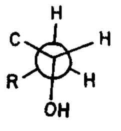
TABLE 7

Temperature Coefficient for the Conversion of Alcohols over Tungsten Oxides

Alcohol	Temperature coefficient (kcal/mol) for pretreatment	
	Oxygen	Hydrogen
2-Octanol	24	ca. 28
4-Methyl-2-pentanol	22	—
($c + t$)-2-Methylcyclohexanol	43	—
Cyclohexanol	40	—

The value for the hydrogen-pretreated sample is questionable because the Arrhenius plot did not give a good straight line relationship. These values are calculated from rate data obtained at a later time on stream and correspond to at least a partially reduced catalyst. The reaction was considered to be a zero-order reaction.

In summary, it appears that the oxygen-pretreated tungsten oxide has an alkene selectivity for acyclic 2-ol dehydration that is very similar to that of alumina (*7*). This selectivity results in a *cis*-2-/*trans*-2- ratio that is much greater than the thermodynamic value. When the tungsten oxide was reduced with hydrogen the *cis*-2–*trans*-2- ratio changed from the 2.5 to 4.0 range to a value of 0.6 to 0.7. This suggests that as oxygen anions are removed from the vicinity of the catalytic site, the transition state **II** (or a skewed analog of **II**) leading to the *trans* isomer becomes the favored conformation. Bartsch *et al.* (*8*) have recently reported that, for the base-catalyzed alkene formation from tosylates, base association increased the percentage of 1-alkene formation and the *cis*-2-/*trans*-2- ratio over that obtained for the undissociated base. The results strongly suggest that the alkene selectivity from dehydration of alcohols is sensitive to the site geometry and that the high *cis*-/*trans*- ratio may be obtained when the oxygen bases are crowded closely together around the catalytic site. Otherwise, it would appear that the alkene selectivity would have to be associated with the lower unsaturated coordination of the metallic ion.



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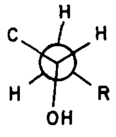

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