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Selectivities of Rare Earth Oxide Catalysts for Dehydration of Butanols

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The catalytic dehydration of 2-propanol, 1-butanol, and 2-butanol over La_2O_3, CeO_2, Pr_6O_{11}, Sm_2O_3, Eu_2O_3, Dy_2O_3, Ho_2O_3, and Yb_2O_3 is studied. Because of the gradual variation of the general properties of 4*f* oxides, the former group has been considered a likely series to analyze the existence of definite correlations between alkene distribution and catalyst properties, often reported in the literature. According to our study, the effect of temperature on product distribution may strongly restrict the validity of such correlations. This point is discussed on the basis of the linear relationships found here between E_a and log A.

INTRODUCTION

According to most papers dealing with alcohol dehydration over polar catalysts, their acid–base properties seem to be a very important factor in the determination of the reaction mechanism (*1*). The olefin distribution may be related to the elimination mechanism (*2*). Therefore, these three aspects of the catalytic dehydration of alcohols—acid–base properties of catalysts, reaction mechanism, and product distribution—are often correlated. Thus, Siddhan (*3*) suggests the existence of a correlation between catalyst basicity and terminal alkene formation. The comparison of the acid–base properties of catalysts has also been carried out on the basis of selectivity data (*4, 5*).

However, some of these correlations are of doubtful validity, because they are based exclusively on product distribution measurements carried out over a definite range of temperatures or even at a single temperature. In our opinion, selectivity data obtained in this way cannot be considered, in general, a suitable parameter to describe the behavior of catalysts or to define the operating mechanism. Alkene distribution may depend strongly on the temperature and, therefore, our conclusions might well be determined by the selected temperature, the choice of which is seldom based on specific scientific criteria.

Continuing the discussion on metal oxide selectivity initiated in previous papers (*6*), we will analyze here the meaning of the abovementioned correlations, studying the dehydration of 2-propanol, 1-butanol, and 2-butanol on several 4*f* oxides. The known valence stability shown by most lanthanide elements, as well as the definite sequence followed by the properties of their sesquioxides throughout the series, suggested applying that discussion to them.

EXPERIMENTAL

The series of 4*f* oxides comprising La_2O_3, CeO_2, Pr_6O_{11}, Sm_2O_3, Eu_2O_3, Dy_2O_3, Ho_2O_3, and Yb_2O_3 were prepared in our laboratory by calcination in air, at 873 K, of the corresponding hydroxides. The oxides were characterized by X-ray diffraction, surface area, and pore size distribution measurements (*7, 9, 15*). Their specific areas ranged from 15.1 to 40.5 $m^2 g^{-1}$, and no microporosity was observed.

The decompositions of 2-propanol, 1-butanol, and 2-butanol were the test reactions studied. These alcohols, Merck A.R. grade, were used without further purification.

The catalytic activity measurements

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TABLE 1

Kinetic Parameters for Dehydration of 2-Propanol, 1-Butanol, and 2-Butanol on 4*f* Oxides

	2-Propanol						2-Butanol					
	HT[a]		LT[b]		1-Butanol		1-Butene		*cis*-2-Butene		*trans*-2-butene	
	E_a[c]	A[d]	E_a[c]	A[d]	E_a[c]	A[d]	E_a[c]	A[d]	E_a[c]	A[d]	E_a[c]	A[d]
La_2O_3	64	2.4×10^{22}	105	3.1×10^{25}	171	2.3×10^{29}	136	1.5×10^{28}	128	4.2×10^{26}	131	6.7×10^{26}
CeO_2	74	7.6×10^{22}	74	7.6×10^{22}	131	1.6×10^{26}	123	2.3×10^{26}	117	1.5×10^{25}	122	3.9×10^{25}
Pr_6O_{11}	51	2.2×10^{21}	87	1.0×10^{24}	120	4.4×10^{25}	122	6.5×10^{26}	125	6.8×10^{25}	128	1.4×10^{26}
Sm_2O_3	59	1.2×10^{22}	117	4.0×10^{26}	175	3.3×10^{29}	120	8.4×10^{26}	116	2.4×10^{25}	118	4.0×10^{25}
Eu_2O_3	56	3.9×10^{21}	108	3.6×10^{25}	135	6.1×10^{26}	117	3.3×10^{26}	113	1.8×10^{25}	115	2.2×10^{25}
Dy_2O_3	—	—	—	—	137	1.2×10^{27}	125	3.8×10^{27}	126	6.1×10^{26}	127	5.9×10^{26}
Ho_2O_3	—	—	—	—	166	1.4×10^{29}	116	6.9×10^{26}	116	2.3×10^{25}	116	2.1×10^{25}
Yb_2O_3	—	—	—	—	131	4.0×10^{26}	120	1.2×10^{27}	114	1.2×10^{25}	116	1.6×10^{25}

[a] High-temperature kinetic parameters.

[b] Low-temperature kinetic parameters.

[c] Activation energy (kJ mol^{-1}).

[d] Preexponential factor (molec. s^{-1} m^{-2}).

were carried out in a flow reactor (*8*), at low conversions. We operated in pseudo-zero-order conditions and the influence of the diffusion phenomena was always avoided. The analysis of the reaction products was performed by gas chromatography.

RESULTS

From catalytic activity measurements obtained as previously described, we have calculated the usual kinetic parameters E_a and A for the dehydration of 2-propanol, 1-butanol, and 2-butanol over the series of 4*f* oxides. These are reported in Table 1. The oxides were also active in alcohol dehydrogenation (*9*). Within the experimental range of temperature, 623–773 K, the alkenes included in Table 1 are the only significant products of reaction in addition to those of dehydrogenation.

For 2-propanol dehydration, high temperature (HT) and low temperature (LT) kinetic parameters are given. These symbols account for the change of slope found around 673–693 K in the corresponding Arrhenius plots (*9*).

From the data reported in Table 1 we have calculated the alkene distribution arising from the dehydration of 2-butanol (Table 2). Since the formation of the three butenes takes place with rather similar activation energies, the temperature has little effect on the product distribution. Nevertheless, it is worth mentioning that among the sesquioxides studied here the highest percentage of 1-butene (Hofmann olefin) corresponds to holmia and ytterbia, and the lowest to lanthana. This is the exact opposite of what is suggested in the literature (*3*) on the basis of the bulk basicity of 4*f* sesquioxides increasing from Lu to La (*10*). On the other hand, no definite variations of selectivity can be observed along the whole series of oxides; in fact different sequences are found within the experimental range of temperatures.

TABLE 2

Alkene Distribution Corresponding to the Dehydration of 2-Butanol over 4*f* Oxides

	423 K[a]		473 K		573 K		673 K		773 K	
	1-B[b]	C/T[c]	1-B	C/T	1-B	C/T	1-B	C/T	1-B	C/T
La_2O_3	66.0	1.5	70.5	1.3	76.7	1.2	80.4	1.1	82.8	1.0
CeO_2	61.7	1.3	64.5	1.1	68.2	0.9	70.7	0.8	72.3	0.7
Pr_6O_{11}	93.7	1.1	92.7	1.0	90.9	0.9	89.4	0.8	88.2	0.8
Sm_2O_3	85.4	1.2	86.5	1.1	88.0	1.0	88.9	0.9	89.5	0.9
Eu_2O_3	80.1	1.3	81.3	1.3	83.0	1.2	84.1	1.1	84.9	1.1
Dy_2O_3	85.7	1.5	84.9	1.4	83.6	1.4	82.6	1.3	81.9	1.3
Ho_2O_3	94.3	1.0	94.3	1.0	94.3	1.0	94.2	1.0	94.2	1.0
Yb_2O_3	91.5	1.4	92.6	1.3	94.0	1.2	94.8	1.1	95.3	1.0

[a] Temperature in K.

[b] Percentage of 1-butene.

[c] *Cis–trans* ratio.

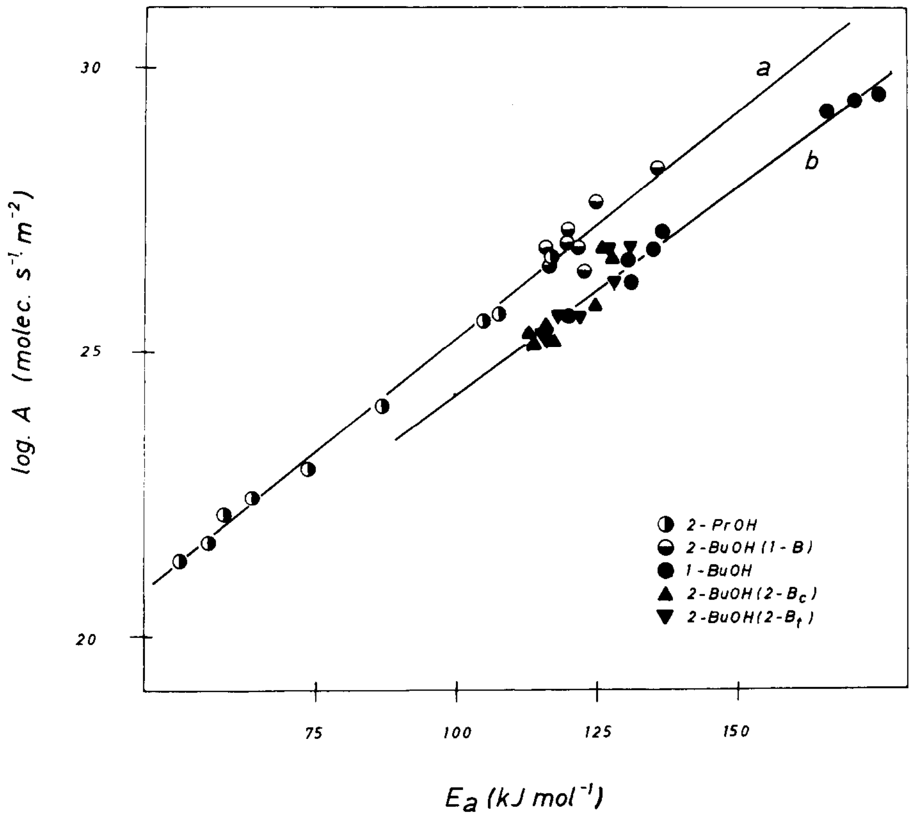

FIG. 1. Linear relationships E_a vs log A for the dehydration of 2-propanol, 1-butanol, and 2-butanol over 4*f* metal oxides.

The data in Table 1 also show no clear correlation along the series as regards activation energy. However, two linear relationships similar to those reported by Galwey (*11*) were found here. The first one, line a in Fig. 1, includes kinetic parameters for the dehydration of 2-propanol and 2-butanol to 1-butene. The second one, line b, corresponds to data for dehydration of 1-butanol and 2-butanol to *cis* and *trans* 2-butenes. The slopes (*e*) and intercepts (*B*) corresponding to these straight lines are shown in Table 3.

DISCUSSION

Concerning the activation energy data included in Table 1, a concerted E_2-type elimination mechanism seems to be the most likely. In effect, the formation of 1- and 2-butenes from 2-butanol takes place with analogous activation energies and, in addition, 1-butene was the only alkene found in 1-butanol dehydration. Likewise, the similarity of the activation energies for

TABLE 3

Characteristic Parameters Corresponding to Several Linear Relationships between E_a and Log A

	e	σ_e[a]	B	σ_B[b]	β(K)
Straight line a	0.080	0.001	17.14	1.298	655
Straight line b	0.074	0.001	16.86	1.555	712
C_4-alcohol[c]	0.073	0.006	19.45	0.661	720
C_5-alcohol[c]	0.077	0.004	17.94	0.361	677
BPO_4[d]	0.108	0.006	16.73	1.087	487

[a] Standard deviation of slope.

[b] Standard deviation of intercept.

[c] Data corresponding to Al_2O_3 reported by Galwey (*11*).

[d] Calculated from Table 5.

2-butenes formation (*cis* and *trans*) suggests that the elimination must go primarily through a syn-E_2 mechanism. According to the model of Knözinger *et al.* (12), anti-elimination would give rise to a higher activation energy for *trans* 2-butene formation, especially over low porosity catalysts like those used here.

When the alcohol dehydration takes place through a concerted mechanism, the activation energy is determined by many factors, some of them operating in opposition. With regard to the alcohol structure, hyperconjugation, steric strains, and inductive effects on C_α and C_β may modify that kinetic parameter. Acid–base and structural surface properties ought to be considered in relation to the catalysts. Also, the preparation methods and pretreatments of catalysts may modify their behavior (13, 14). The former factors deal with the alcohol and catalysts independently considered, but the behavior of catalysts is actually defined by the surface state during the catalytic process and, therefore, it will be determined by the reactant–catalyst interaction at the reaction conditions. Concerning this last factor, our own results from the infrared study of the 2-propanol–Yb_2O_3 interaction show that the thermal change of this adsorbed phase depends on the conditions at which the alcohol–oxide interaction takes place (15).

Since the relative weight of those factors on the activation energy values is difficult to evaluate, no well-defined correlation of this parameter is to be expected when the dehydration of an alcohol on a series of catalysts or vice versa is compared. Furthermore, the difficulties that arise from the interpretation of the meaning of the activation energy in heterogeneous catalysis may also complicate the aforementioned correlations. In our case, the absence of any definite trend of activation energy along the whole series of 4*f* oxides agrees with such considerations.

Likewise, it is not to be expected that selectivity data will be related in general to the chemical constitution of catalysts in a simple way. However, in alkene distribution studies from alcohol dehydration, alumina, and thoria are often considered representative catalysts of two extreme behaviors. In accordance with Thomke's opinion (16) the most substituted alkene (Saytzeff olefin) is preferential on alumina, whereas over ThO_2 the least substituted one (Hofmann olefin) is the principal product. Likewise, regarding the *cis–trans* ratio (C/T), high *cis* preference is associated with alumina (3).

The former statements, which imply a generalization of results obtained from specific alcohols and conditions, may lead to certain confusion and perhaps to error. Table 4 shows the temperature dependence of the alkene distribution for 2-butanol and 2-pentanol dehydration on Al_2O_3. These data were calculated from the kinetic parameters reported by Knözinger *et al.* (12), where the experimental range of temperatures was 428–471 K for 2-butanol and 476–522 K for 2-pentanol. Therefore data included in Table 4 correspond to a temperature range wider than the experimental one. This extrapolation has been carried out for the purpose of comparison since the activity of more basic catalysts is generally studied at higher temperatures (16, 17) and, therefore, the meaning of those data is exclusively formal. It is worth mentioning that, at the specific temperature of 673 K, the C/T ratios corresponding to 2-butanol dehydration on Al_2O_3 (Table 4) and

TABLE 4

Dehydration of 2-Butanol and 2-Pentanol on Alumina[a]

	423 K[b]		473 K		573 K		673 K		773 K	
	1-A[c]	C/T[d]	1-A	C/T	1-A	C/T	1-A	C/T	1-A	C/T
2-ButOH	—	10.0	—	5.2	—	2.0	—	1.0	—	0.6
2-PentOH	59	7.1	45	4.9	26	2.8	16	1.9	11	1.4

[a] Alkene distribution calculated from kinetic parameters reported in Ref. (12).

[b] Temperature in K.

[c] Percentage of 1-alkene.

[d] *Cis–trans* ratio.

4*f* oxides (Table 2) are similar in spite of the known differences in their general chemical behavior.

According to Table 4, the temperature exerts a strong influence on the alkene distribution. Thus, in 2-pentanol dehydration the C/T ratio ranges from 7.1 to 1.4 and a greater temperature effect is found for 2-butanol dehydration. Likewise, the percentage of 1-pentene varies greatly, being higher than 50% (Hofmann preference) at 423 K.

Recently, Galwey (*11*) has reported the existence of two linear relationships between the activation energy and the logarithm of the preexponential factor corresponding to the dehydration of several butanols and pentanols studied by Knözinger *et al.* (*12*). This gives a clear understanding of the results shown in Table 3. In effect, as is well known, these relationships imply the existence of an isokinetic temperature, β, and, therefore, if two reactions take place with different activation energy, the ratio of their two reaction rates will be greater or lesser than unity depending on whether $T > \beta$ or $T < \beta$. This can be seen in Fig. 2, which shows the

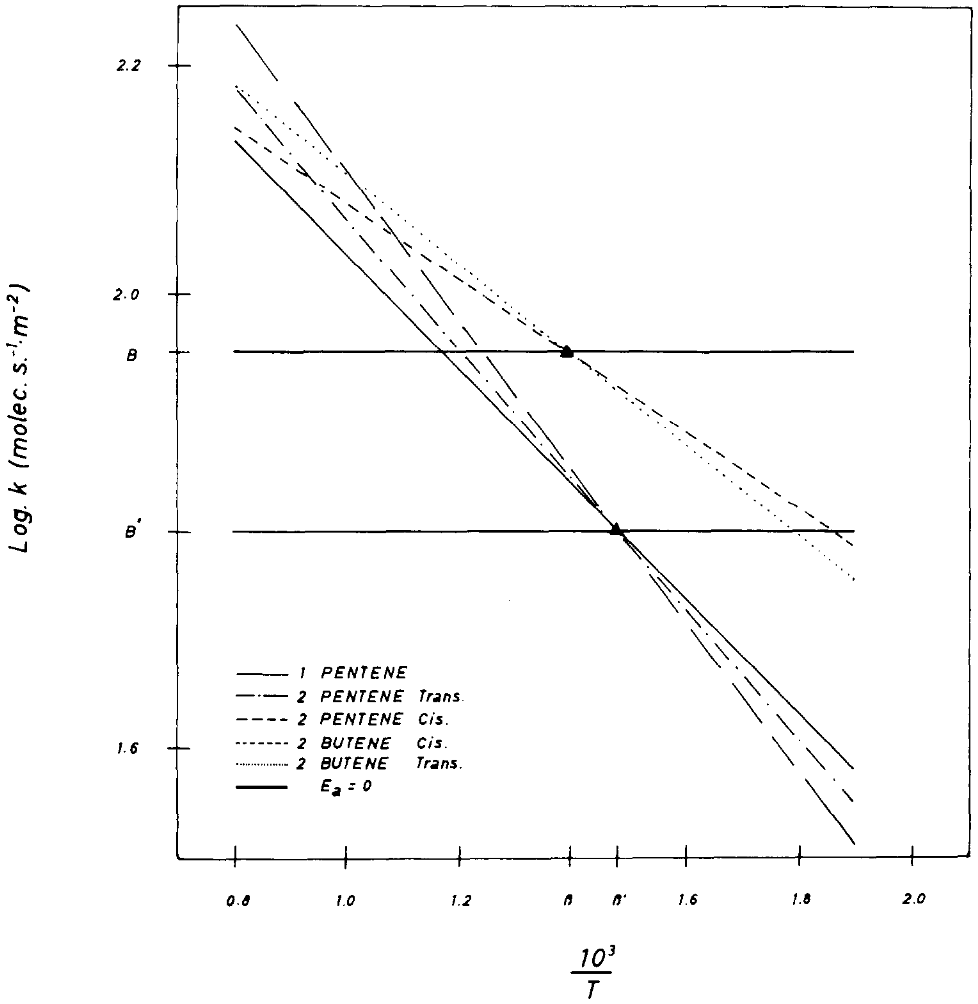

FIG. 2. Arrhenius plots including isokinetic temperature ranges for 2-butanol and 2-pentanol dehydration on Al_2O_3. Data taken from Refs. (*11*) and (*12*).

Arrhenius plots corresponding to the formation of the different alkenes from 2-butanol and 2-pentanol dehydration. Slopes (*e*) and intercepts (*B*) for the compensation straight lines reported by Galwey (*11*), summarized in Table 3, and activation energies from Ref. (*12*) were the bases of this figure.

The analysis of Fig. 2 and Table 4 suggests that from selectivity data obtained at a single temperature, or in a short range, it is not justified to ascribe a specific product distribution to the catalyst. On the other hand, we must point out that the data included in Table 4 were obviously calculated by supposing there were no changes in the reaction mechanism and, even in that case, very different alkene distributions can correspond to the same mechanism depending on the selected temperature. The difficulties of using the comparison of reaction rate data at a single temperature to draw mechanistic conclusions were pointed out by us a few years ago (*6*) and again recently (*18*).

As a result of the former statements, some of the conclusions assumed in recent papers on this subject become doubtful. Thus, Jewur and Moffat (*5*) from the dehydration of several alcohols on a series of boron phosphate catalysts conclude that a correlation exists between surface acidity and the preferential orientation to the most substituted alkene (Saytzeff orientation). Likewise, the authors suggest that high *cis* preference would be related to the catalysts with lower acidity. Nevertheless, a single temperature (423 K) was used for carrying out their study. In our opinion, it is not obvious that the effect of the temperature on the product distribution would be the same for every catalyst and, therefore, it is possible that several correlations between the properties of the catalyst and alkene distribution would be found depending on the selected temperature.

Analogous difficulties could be mentioned when rate constants for 1-propanol dehydration over a series of boron phosphate catalysts are correlated to their total surface acidity (*19*). Temperatures ranging from 443 to 468 K were studied. However, from the rate constants at 448 K and activation energies reported by the authors, we could calculate the corresponding preexponential factors (Table 5), finding a linear relationship between E_a and log A. The characteristic parameters e and B, as well as the isokinetic temperature, β = 487 K, are included in Table 3. According to Fig. 2, if the authors had studied the catalytic activity at slightly higher temperatures ($T >$ 487 K), they would have arrived at quite the opposite conclusion.

For the 4*f* oxides studied here, because of the small effect of the temperature on the butenes distribution, 1-alkene preference exists in a wide range of temperatures. This preference would be related to the higher preexponential factor for 1-butene formation. In Fig. 1 we can see that the points lying on straight line a correspond to kinetic parameters for the elimination of a hydrogen atom from a methyl group, whereas straight line b, with lower intercept, includes data corresponding to reactions which imply the elimination of a hydrogen atom from a $-CH_2-$ group, less acid and more sterically hindered than the $-CH_3$ group.

In summary, in spite of the known sequence that the properties of 4*f* sesquiox-

TABLE 5

Kinetic Parameters for *n*-Propanol Dehydration on Several Boron Phosphates[a]

Catalyst	E_a (kJ mol^{-1})	A (molec. s^{-1} m^{-2})
BPR-1 (311°C)	64	4.7×10^{23}
BPR-2 (311°C)	94	1.3×10^{27}
BPR-4 (311°C)	72	4.9×10^{24}
BPR-1 (421°C)	62	1.5×10^{23}
BPR-2 (421°C)	91	4.0×10^{26}
BPR-1 (536°C)	95	6.5×10^{26}
BPR-2 (536°C)	124	1.1×10^{30}

[a] Data calculated from Ref. (*19*).

ides show along the whole series, neither activation energy nor selectivity correlations could be found. These results, as well as those previously discussed, suggest that the use of selectivity data to draw mechanistic conclusions or to compare the behavior of catalysts has obvious restrictions. Correlations considered well established like that of high C/T $\rightsquigarrow$ antielimination (*3*) often based on the data of Knözinger *et al.* (*12*), may be accepted only if we take into account that the catalytic activity measurements were carried out in that work far below the isokinetic temperature. If this reference, β, had not been considered a concrete value of C/T ratio would have had no definite meaning. According to Ref. (*12*), higher activation energy ought to correspond to *trans* 2-alkene formation when antielimination operates, and this requirement only gives rise to $C/T > 1$ at $T < \beta$. In spite of the importance of this point, most papers about this subject have not considered it, due to the lack of the necessary reference for carrying out their selectivity discussions.

As the existence of linear relationships like those found in this paper seems to be a fairly common occurrence in alcohol dehydration over polar catalysts (Ref. *11* and references therein, *20*), an analysis of its possible existence, as well as the establishing of its characteristic parameters e and B, may offer wider criteria to discuss the selectivity problems.

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