JOURNAL OF CATALYSIS 57, 167–176 (1979)

The Role of Surface Acidity of Boron Phosphate in the Activity and Selectivity of the Dehydration of Alcohols

S. S. JEWUR AND J. B. MOFFAT[1]

Department of Chemistry and Guelph–Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Received July 10, 1978; revised November 13, 1978

A comparison between the activity and selectivities of dehydration of 2-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol has been made with the surface acidity of boron phosphate catalysts of compositions ranging from P/B = 0.4 to 1.4. The activity and the product distribution of the dehydration reactions of these alcohols were found to be sensitive to the change in the surface acid properties of the boron phosphate catalysts. The concentrations of *trans*-2-butene and 2-methyl-2-butene increase with increasing surface acidity, while those of the various remaining products show an inverse relationship to the acidity. The results are interpreted through a dominant carbonium ion mechanism with the possibility of an additional subsidiary process.

INTRODUCTION

A variety of mechanisms has been proposed for elimination reactions, and in particular those involving the vapor phase dehydration of alcohols (*1*). Of these mechanisms, those involving a carbonium ion (E1), a carbanion (E1cb), or a concerted elimination (E2) are the most common. Of course, each of these mechanisms may not be discrete in the sense that they represent only three possibilities in a broad spectrum of mechanisms. Thus, in a vapor phase elimination the first two mechanisms will be associated with energy profiles possessing two maxima, while the latter mechanism will involve only one such maximum. The relative heights of these two barriers will then determine, at least in part, the extent of the mixing of two or even more of such mechanisms. The presence of a catalytic surface may, of course, add a further complexity to the energy profile and, given the probable energetic heterogeneity of the surface, may produce a wide variety of such energy profiles in a given dehydration experiment.

These elimination mechanisms can be further divided into *syn*- and *anti*-elimination modes depending, for example in the case of dehydration of alcohols, on the stereochemical orientation of the leaving hydrogen with respect to the hydroxyl group in different conformations of the alcohol molecules.

Although β-elimination can be considered to be the common factor in the aforementioned mechanisms, the concerted γ-elimination with migration of β-hydrogen (or any other β-substituent) must be added to any list of possible elimination mechanisms (*2–5*).

Information on the primary products of the decomposition of alcohols can prove useful in suggesting possible intermediates of dehydration reactions and consequently in postulating mechanisms (*1*, *2*, *5–7*).

---

[1] To whom correspondence should be sent.

0021-9517/79/040167-10$02.00/0

Thus, in investigations of the dehydration of alcohols, the isomeric distribution of olefins has been taken as an important criterion in characterizing the surface properties of the catalysts and also in discussing the surface–alcohol interaction during the dehydration.

The catalytic decomposition of alcohols has been the subject of investigation for a number of years. Fortunately, several excellent reviews on the topic are available, one on elimination reactions in general by Noller and Kladnig (*1*) and another by Knözinger specifically dealing with the dehydration of alcohols (*8*). The interest in alcohol decomposition as a probe reaction for catalytic surfaces has continued since the latest of these reviews was published.

Previous work from this laboratory (*9–14*) has demonstrated the presence of acidic sites on the surface of boron phosphate. The presence of a substantial number of Brønsted sites has been implied from the results of deuterium exchange experiments (*9*) and from studies of the oxidation of iodide ions in the liquid phase (*10*). The rate of dehydration of 1-propanol on boron phosphate was found to be related to the number of surface acid sites and an increase in the pretreatment temperature of the catalyst decreased both the concentration of acid sites and the rate of dehydration (*11–12*). Similarly, Tada *et al.* (*15*) and Tada and Mizushima (*16*) have found a direct relationship between the dehydration activity for 1-butanol and the surface acidity on aluminum phosphate and on boron phosphate.

In view of the importance of acidic and basic centers in promoting the dehydration of alcohols, one can expect that the acid–base properties of the catalyst surface will have a significant effect on the product distribution as well as on the dehydration mechanism. Accordingly, the purpose of the present work is twofold: (1) to examine the primary decomposition product distributions from the dehydration of alcohols in order to elucidate both the mechanisms and the surface properties of the catalyst and (2) to perform these experiments on nonstoichiometric boron phosphate samples with a variety of phosphorus/boron molar ratios (P/B) to determine the manner in which the changes in P/B influence both the surface acidity and the product distributions. For this purpose 2-butanol and its derivatives, 2-methyl-2-butanol and 3-methyl-2-butanol, were chosen as the alcohols for study, and the isomerization of 1-butene, the chemisorption of ammonia, and the titration with *n*-butylamine were employed as methods for the estimation of surface acidity.

EXPERIMENTAL METHODS

1. *Microcatalytic Pulse Reactor*

The dehydration of 2-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol, and the isomerization of 1-butene were carried out in a microcatalytic pulse reactor. The basic features of the apparatus used in our work are similar to those discussed by Galeski and Hightower (*17*). The reactor system used in the present work is a modified version of that previously described (*11*).

A regulated flow of helium, 30 ml/min was saturated at a known temperature with the alcohol and this gaseous mixture was passed through a bypass doser. The alcohol vapors diluted with helium which are trapped into the sample loop are then passed over the catalyst (20 mg) held inside a reactor by means of a second stream of helium controlled at the desired flow rate (300 ml/min). The reactions were studied at 150°C. The shape of the reactant pulses and the product slugs were analyzed by a thermal conductivity detector placed between the bypass doser and the reactor. The products were trapped in a U tube placed in liquid nitrogen. The temperature of the U tube was raised to a particular level depending upon the boiling points of the product components to be analyzed before they are swept into the appropriate columns of the gas chromatograph.

The gas chromatographic separation of 1-butene, *trans*-2-butene, 3-methyl-1-butene, *cis*-2-butene, 2-methyl-1-butene, and 2-methyl-2-butene, with retention times 10.5, 12, 12.8, 13.6, 18.5, and 22 min, respectively, was obtained by a 40 ft × ¼-in. column of 30% β,β'-oxydipropionitrile on 40/60 mesh chromosorb P at room temperature with a 70 ml/min flow of helium. The quantitative analysis of the pulse concentration as well as that of the unreacted alcohols was made using a 6 ft × ¼-in. column of 20% carbowax 20M (TPA) on 60/80 mesh chromosorb W.

2. Catalysts and Reactants

Eight different samples of boron phosphate with varying phosphorus to boron (P/B) molar ratios ranging from 0.4 to 1.4 were prepared from boric and phosphoric acid by the method described previously (*18*). The samples prior to the thermal treatment in vacuum are designated as "unpretreated," while those evacuated at an elevated temperature for a certain time period are labeled as "pretreated." In the present work only samples pretreated at 400°C for 8 hr were employed. Preliminary dehydration experiments were done with 2-butanol by varying the helium flow rate, the range of particle size of the pretreated samples, and the weight of the catalyst in order to determine suitable reaction conditions. A helium flow of 300 ml/min, particle sizes of boron phosphate of 120/150 mesh, and a catalyst weight of 20 mg were used in the entire work.

2-Butanol and 2-methyl-2-butanol both were Baker analyzed reagent grade. 3-Methyl-2-butanol was purchased from Matheson, Coleman and Bell. All the three alcohols were found to be chromatographically pure and were used without further purification. 1-Butene was obtained from Matheson of Canada Ltd.

3. Surface Acidity Determination

Two methods were employed to obtain some indication of the surface acidity, namely, titration with 0.01 *M* *n*-butylamine (Fischer Scientific Company, certified grade) solution in benzene (A.R. grade), in the presence of a series of Hammett indicators, and measurement of the chemisorption of ammonia (Matheson, anhydrous) gravimetrically using a quartz spring balance. The catalyst samples were evacuated at 200°C for 3 hr to remove adsorbed surface impurities prior to the equilibration of the catalysts with 15 mm pressure of ammonia at room temperature for 24 hr. The system was then evacuated until there was no further weight loss. The isomerization of 1-butene has also been used as an indicator reaction to probe the acidity of the catalyst. One milliliter of 1-butene was injected into the reactor held at 180°C through a helium carrier gas flow of 164 ml/min. The isomerization products were trapped and analyzed as described earlier.

RESULTS

1. Product Distribution

1.1. Dehydration of 2-butanol. The conversion of 2-butanol on a constant weight of boron phosphate catalyst of different composition varies from 2 to 24%. 2-Butanol on dehydration produces 1-butene, *trans*-2-butene, and *cis*-2-butene. No evidence for dehydrogenation products was found. In Fig. 1, the composition of the decomposition product and the ratio of *cis*-2-butene to *trans*-2-butene is plotted as a function of P/B. The thermodynamic equilibrium compositions of all the alkenes are taken from the reported values by Kilpatrick *et al.* (*19*). The percent concentration of 1-butene, *trans*-2-butene, and *cis*-2-butene remained the same for all the reciprocal space velocities ranging from 10 to 150 mole^{-1} g·min. The percent composition of the alkenes reported in this work is always based on the primary distribution of the dehydration products of alcohols. The concentration of *cis*-2-butene is found to be greater than that of the *trans*-2-butene and at most three times as large as that of 1-butene. The concentrations of both 1-butene and *cis*-2-butane pass through a maximum, while that of *trans*-2-butene passes through a minimum as the value of P/B approaches unity from either side. Consequently the ratio of *cis*-2-butene/*trans*-2-butene exhibits a maximum at P/B = 1 (Fig. 1).

1.2. Dehydration of 2-methyl-2-butanol. 2-Methyl-2-butene and 2-methyl-1-butene are the only observed decomposition products of 2-methyl-2-butanol. The conversion of 2-methyl-2-butanol ranged from 7 to 81%, depending on the P/B ratio, and is greater than that of the remaining two alcohols. In Fig. 2, the product distribution and the ratio of the two alkenes is plotted for the various values of P/B. The concentration of 2-methyl-2-butene is several times greater than that of the 2-methyl-1-butene in the entire range of the catalyst composition. The concentration of 2-methyl-1-butene passes through a maximum while that of the 2-methyl-2-butene passes through a minimum at a P/B = 1. The variation of the concentration of 2-methyl-1-butene and 2-methyl-2-butene with P/B (Fig. 2) is semiquantitatively similar to that of 1-butene (or *cis*-2-butene) and *trans*-2-butene, respectively (Fig. 1).

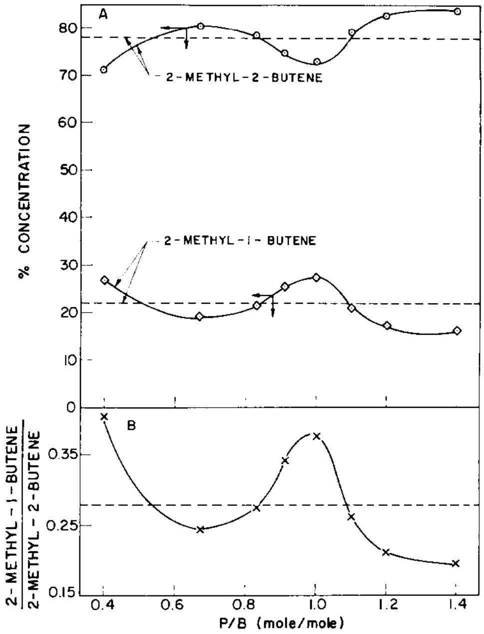

FIG. 2. Experimental (——) and equilibrium (– – –) concentrations of 2-methyl-1-butene and 2-methyl-2-butene (A) and their ratio (B) from the dehydration of 2-methyl-2-butanol on boron phosphate of various compositions.

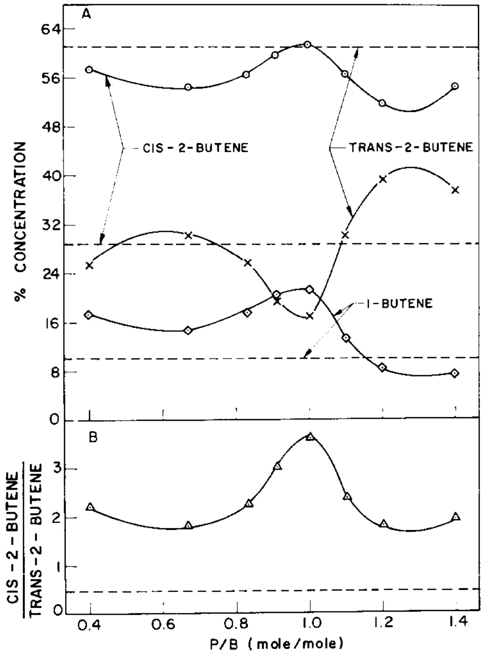

FIG. 1. Experimental (——) and equilibrium (– – –) concentrations of butenes (A) and *cis*-2-butene/*trans*-2-butene ratio (B) from the dehydration of 2-butanol on boron phosphate of various compositions.

1.3. Dehydration of 3-methyl-2-butanol. The conversion of 3-methyl-2-butanol during dehydration over boron phosphate catalysts varies from 3 to 40%. These conversions are slightly greater than those of 2-butanol and substantially lower than those of 2-methyl-2-butanol on the respective compositions of the catalyst. Dehydration of 3-methyl-2-butanol produces 3-

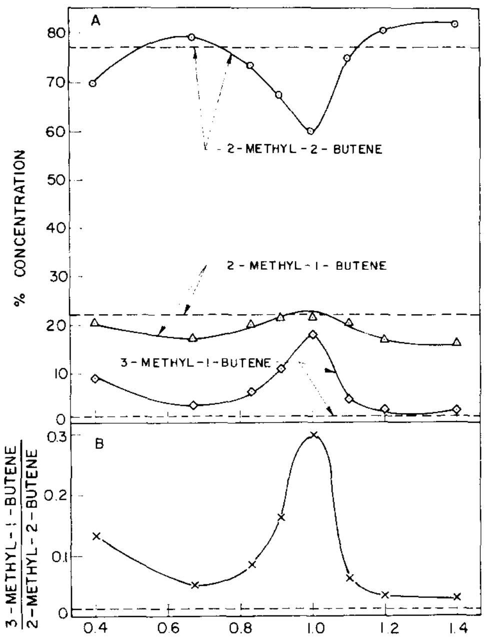

FIG. 3. Experimental (——) and equilibrium (– – –) concentrations of products (A) and the 3-methyl-1-butene/2-methyl-2-butene ratio (B) from the dehydration of 3-methyl-2-butanol on boron phosphate of various compositions.

methyl-1-butene in addition to the dehydration products of 2-methyl-2-butanol. The percent composition of all the three alkenes along with the ratio of 3-methyl-1-butene to 2-methyl-2-butene is plotted as a function of P/B (Fig. 3). The product distribution follows the order 2-methyl-2-butene ≫ 2-methyl-1-butene > 3-methyl-1-butene in the entire range of the catalyst compositions studied. The percent concentrations of 3-methyl-1-butene and 2-methyl-1-butene are found to show a maximum at P/B = 1, and the formation of 2-methyl-2-butene is minimum at this composition.

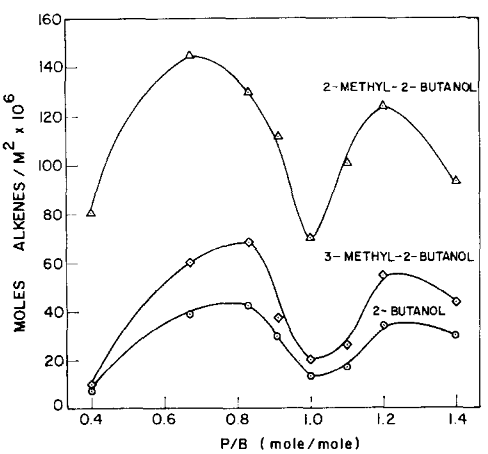

FIG. 4. Specific dehydration activities of the alcohols on boron phosphate of various compositions.

2. Activity of Boron Phosphate for the Dehydration of the Model Alcohols

The total concentration of the alkenes produced from an individual alcohol, expressed in the form of moles × 10^6 per meter square, are referred to as specific catalytic activities for the dehydration reaction. The specific catalytic activities of the dehydration of 2-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol are plotted as a function of the composition of boron phosphate in Fig. 4. All the dehydration reactions were carried out under identical experimental conditions in order to permit comparison of the reactivity of these alcohols. The concentration of each pulse was maintained at $(6.1 \pm 0.2) \times 10^{-5}$

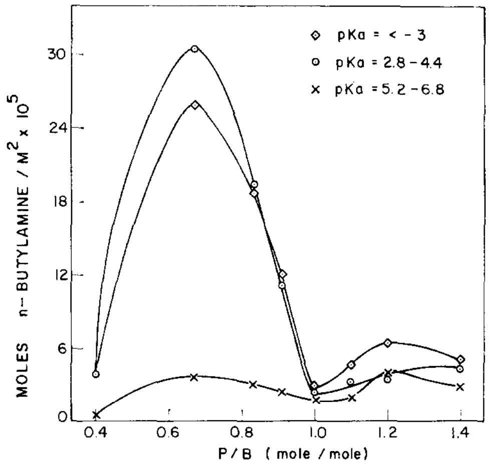

FIG. 5. Concentrations of surface acid sites on various acid strengths as a function of P/B as measured by butylamine titration.

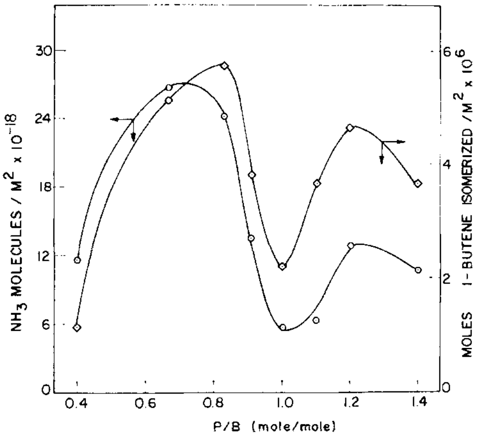

FIG. 6. Surface acidity of boron phosphate as measured by the irreversible adsorption of ammonia and the isomerization of 1-butene on catalysts with different P/B values.

moles throughout this work. The reactivity of the alcohols towards dehydration on boron phosphate catalysts follows the sequence 2-methyl-2-butanol > 3-methyl-2-butanol > 2-butanol. The dehydration activities of the catalysts with P/B = 0.8 and 1.2 are maximum and those at approximately P/B = 1 and P/B = 0.4 are minimum.

3. Surface Acidities of Boron Phosphate

Figure 5 gives the distribution of acid strengths and their densities for the various compositions of boron phosphate catalyst. The densities of the acid sites in the ranges of less than −3 and 2.8 to 4.4 are considerably greater for the catalyst composition, $0.4 < P/B < 1$ compared to those of the catalysts with $P/B > 1$. The acid concentrations in the pK_a range from 5.2 to 6.8 show two maxima, one around P/B = 0.7 and the other at P/B = 1.2.

Figure 6 shows the variation in the acid site densities as determined by measuring the chemisorption of ammonia and also by carrying out the isomerization of 1-butene on the catalysts. The amount of irreversibly chemisorbed ammonia, the amount of 1-butene isomerized, and the surface acid densities as measured using Hammett indicators on various compositions of boron phosphate show reasonably good semiquantitative agreement.

DISCUSSION

There are a number of features, clearly recognizable from the experimental data, which may be used in clarifying the mechanism by which the present alcohols are dehydrated on boron phosphate.

(i) The dehydration activity for the three alcohols is largest with 2-methyl-2-butanol and smallest for 2-butanol for all catalyst compositions (Fig. 4). Since carbonium ion reactivity follows the order tertiary > secondary > primary, this observation is consistent with an E1 mechanism.

(ii) The dehydration of 2-methyl-2-butanol produces two products, 2-methyl-2-butene and 2-methyl-1-butene, the former in larger quantities than the latter, and both in concentrations approximately the same as those expected at equilibrium (Fig. 2). This observation is also suggestive of a carbonium ion or E1 mechanism, although an E2 mechanism is not precluded.

(iii) The dehydration of 3-methyl-2-butanol produces three products, 2-methyl-2-butene, 2-methyl-1-butene, and 3-methyl-1-butene, in order of decreasing concentration (Fig. 3). The observed relative order of concentrations of the olefins is identical with that expected at equilibrium. These results also favor the E1 mechanism. With all three alcohols, the olefin with the greater number of alkyl groups predominates, that is, Saytzeff orientation is favored.

(iv) The quantities per square meter of ammonia chemisorbed (Fig. 6), of 1-butene isomerized (Fig. 6), and of butylamine titrated (Fig. 5), all vary in a semiquantitatively similar manner as the composition of the catalyst is varied. With all three methods, minima appear at P/B equal to 1.0, and maxima appear at P/B values of approximately 0.7 and 1.2. Thus, at least within the confines of the capabilities of the particular measurement method, the total number of acid sites, both Brønsted and Lewis, is largest for boron phosphate of nonstoichiometric composition.

(v) The dehydration of 2-butanol produces three products, *cis*-2-butene, *trans*-2-butene, and 1-butene, in order of decreasing concentration, whereas at equilibrium the order of decreasing amounts is expected to be *trans*-2-butene, *cis*-2-butene, and 1-butene (Fig. 1).

(vi) The concentrations of *trans*-2-butene formed from 2-butanol (Fig. 1) and of 2-methyl-2-butene produced from both 2-methyl-2-butanol (Fig. 2) and 3-methyl-2-butanol (Fig. 3) vary in a similar manner showing minima at P/B equal to 1.0.

(vii) The concentrations of *cis*-2-butene, 1-butene, 2-methyl-1-butene, and 3-methyl-1-butene show similar trends with changes in catalyst composition, with maxima appearing at a P/B value of approximately 1.0.

The similarities observed in the behavior of the acidity measurement data (Figs. 5 and 6) and the specific dehydration activity of all three alcohols (Fig. 4) as a function of catalyst composition demonstrate that the catalytic activity is related to the number of acidic sites of the catalyst. However, since none of the methods employed to measure the numbers of acidic sites is capable of distinguishing between Brønsted and Lewis sites, it is not possible to determine which of these is the more effective in the present reactions. Of course, it is not impossible that only a portion of the acidic sites present on the surface of the catalyst are active in the reactions studied here, but the information available at present is insufficient to permit further elaboration of this aspect. However, the similarity observed in the results obtained from the three methods employed for the estimation of acidity and the correlation observed between the density of acid sites and the dehydration activities provides strong evidence for a carbonium ion or E1 mechanism in the dehydration of the alcohols considered here. It must be again emphasized, however, that an additional mechanism is not precluded.

The product distribution of the dehydration reactions of 2-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol also appears to be dependent upon the acidity of the catalyst (Figs. 1–3, 5, 6). The formation of 1-butene and *cis*-2-butene is favored on the catalysts with smaller numbers of acidic sites. The production of *trans*-2-butene, on the other hand, appears to be more directly determined by the number of acid sites on the catalyst, since the larger this number, the greater the percentage concentration of *trans*-2-butene in the products. The percent conversion of the 2-butanol is also smaller on the catalysts possessing a smaller number of acid sites.

In attempting to explain the observations from the present work, it is of value to compare the results obtained by other workers in the study of the dehydration of the present alcohols on various catalysts. Pines (*2*) has studied the dehydration of 2-butanol on alumina, and has observed a decrease in both the percent composition of *trans*-2-butene and percent conversion of 2-butanol, after neutralization of the acid sites, but the concentrations of 1-butene and *cis*-2-butene were increased with the increase in the amount of sodium in alumina (*2*). The results obtained with 2-butanol on alumina thus show the same relationship with surface acidity as those found with boron phosphate.

Carrizosa and Munuera (*20*) find that 2-butanol decomposes on TiO_2 to produce 16% of the Hofmann olefin (1-butene) and 84% of the Saytzeff products (2-butenes) with a *cis/trans* ratio of 3.5. Carrizosa and Munuera (*20*) suggest that their results for 2-butanol support an E2 mechanism. In comparison, on boron phosphate the *cis/trans* ratio ranges from approximately 1.6 to

3.6, and the percent Hofmann olefin from 7 to 22%. Since stoichiometric boron phosphate produces 22% Hofmann olefin and a *cis/trans* 2-butene ratio of 3.6, it appears that this particular catalyst composition, where P/B = 1.0, is quite similar to that of TiO_2 in respect of acid–base properties.

On alkali cation-exchanged X and Y zeolites (*21*), 2-butanol yields 80 to 85% of the 2-butenes with a *cis/trans* ratio of approximately 1.0 to 1.1. The yield of 2-butenes is similar to that obtained with the boron phosphate catalysts but the *cis/trans* ratio of the 2-butenes is much lower on these zeolites than on boron phosphate. High yields of 2-butenes have also been reported for butene isomerization on weakly acidic zeolites (*22*). On alkali cation-exchanged X and Y zeolites the decomposition of 2-butanol is believed to occur by an E1 elimination (*21*). In contrast with the aforementioned work, on alumina a high *cis/trans* ratio for 2-butenes of approximately 5.9 was obtained, while the quantity of 2-butenes is again high at approximately 70% (*23*). An E2 elimination has been proposed for alcohol dehydration on alumina.

With calcium phosphate (hydroxyapatite), only dehydration of 2-butanol occurred on samples with P/Ca equal to 0.63, but both dehydration and dehydrogenation reactions took place on the stoichiometric solid (i.e., P/Ca = 0.6) (*24*, *25*). With the nonstoichiometric catalyst the *cis/trans* ratio of 2-butenes was 1.46 at 282°C. Dehydration over hydroxyapatite was found to obey the Saytzeff rule and was consistent with an E1 mechanism.

Thomke (*26*) has studied the decomposition of 2-butanol over a number of phosphates, all of commercial origin and therefore presumably of stoichiometric composition. With $Ca_3(PO_4)_2$, BPO_4, $Ba_3(PO_4)_2$, $CaHPO_4$, and $AlPO_4$, approximately 73, 90, 69, 69, and 77%, respectively, of the 2-butenes were obtained from 2-butanol, and *cis/trans* ratios of approximately 1.2, 1.4, 1.8, 1.7, and 1.0, respectively, were measured. The values obtained by Thomke for BPO_4 agree quite well with the present results for a boron phosphate catalyst with P/B equal to approximately 1.2. With $Ca_3(PO_4)_2$, $Ba_3(PO_4)_2$, and $CaHPO_4$ catalysts, an E2 mechanism is favored, while on BPO_4 and $AlPO_4$, the E1 mechanism is calculated to be preferred.

Knözinger *et al.* (*27*) and Pillai and Pines (*5*) studied the dehydration of 2-methyl-2-butanol over alumina and found that 2-methyl-1-butene was the preferred product over 2-methyl-2-butene. With boron phosphate the 2-methyl-2-butene/2-methyl-1-butene ratio varies from 2.5 to 4.0. Figure 2 indicates clearly the distribution of these two alkenes on varying composition of boron phosphate catalyst. The fact that the distribution of the dehydration products of 2-methyl-2-butanol is not comparable with that on alumina (*5*, *27*) suggests that the reaction mechanism on boron phosphate may be different from the one operative on alumina. The variation of percent composition of 2-methyl-2-butene (Fig. 2) resembles that of *trans*-2-butene (Fig. 1) and the similarities can also be observed in the dependence of the formation of 2-methyl-1-butene from 2-methyl-2-butanol and *cis*-2-butene (or 1-butene) from 2-butanol on the composition of boron phosphate.

Carrizosa and Munuera (*20*) find that 2-methyl-2-butanol dehydrates on TiO_2 to favor the Hofmann product, 2-methyl-1-butene, at lower temperatures, but the Saytzeff product, 2-methyl-2-butene, at higher temperatures. For example, at 150°C, 68% of 2-methyl-2-butene is formed. On boron phosphate of various compositions, 70 to 80% of 2-methyl-2-butene was formed. An E2 elimination has been proposed to explain the decomposition of alcohols on TiO_2 (*20*).

The dehydration products of 3-methyl-2-butanol on alumina were found to be 2-methyl-2-butene and 3-methyl-1-butene (*27*). In the present work substantial amounts of 2-methyl-1-butene is also produced from the above mentioned alcohol in addition to the former two alkenes. The general trend in the concentration of 2-methyl-1-butene produced from 3-methyl-2-butanol (Fig. 3), and also from 2-methyl-2-butanol (Fig. 2), and of 1-butene from 2-butanol (Fig. 1) are comparable, although the variation in the concentration of 2-methyl-1-butene is sufficiently small that little emphasis should be placed on this change.

With hydroxyapatite, the decomposition of 3-methyl-2-butanol produced 20 and 10% of 2-methyl-1-butene (the remainder being the two β-elimination products) on the nonstoichiometric and stoichiometric catalysts, respectively (*24*, *29*). On these catalysts the dehydration process is believed to be a nearly concerted elimination. In the present work the concentration of 2-methyl-1-butene ranges from 17 to 23% with the various compositions of boron phosphate catalysts.

Conclusions from the experimental data presented here as well as from comparisons with the results of other workers on various catalysts support the existence of an E1 mechanism in the dehydration of alcohols on boron phosphate. There are, however, some observations in apparent conflict with the hypothesis that the dehydration of alcohols occurs entirely through a carbonium ion mechanism. First, the amount of *cis*-2-butene formed from 2-butanol is considerably greater than that of *trans*-2-butene for all catalyst compositions, and as a consequence the *cis*/*trans* ratio is much larger than that expected at equilibrium. Secondly, the concentrations of *cis*-2-butene, 1-butene, 2-methyl-1-butene, and 3-methyl-1-butene all increase with decreasing numbers of acid sites.

Noller and Kaldnig (*1*) have examined the cases where the *cis*-olefin is favored over the *trans*-olefin and note that the phenomenon is more pronounced on less active catalysts which are more likely to exhibit an E2 mechanism. Knözinger *et al.* (*27*) have suggested that the *cis* preference may be due to a decreased steric hindrance, on the catalystic surface, when the most bulky groups are situated on the same side of the carbon atoms. Noller and Kladnig (*1*) conclude that Pines (*4*) is correct in believing that *cis*-olefin preference is indicative of an E2 mechanism.

Such observations may be applied to the present results in the following manner. Boron phosphate of all compositions examined displays the presence of acidic sites. However, the concentration of acid sites reaches a minimum for catalysts of composition where P/B equals 1.0 (Figs. 5, 6). Further, the activity of a catalyst of this particular composition is less than that of the other compositions studied (Fig. 4). In addition, the quantity of *cis*-2-butene is a maximum for P/B equal to 1.0. This suggests that an E2 mechanism may be significant at such a composition. The observation that *cis*-2-butene is favored (but less so) over *trans*-2-butene with the remaining catalyst compositions implies the operation of both E1 and E2 mechanisms on such surfaces.

In addition with 3-methyl-2-butanol and even more so 2-methyl-2-butanol, with which molecules carbonium ions are more readily formed, the activity of all catalysts increases, the concentrations of the products are more nearly those expected at equilibrium, and it may tentatively be suggested that the participation of the E1 mechanism increases. That the E2 mechanism is still active would then, within the confines of this hypothesis, be evidenced from the deviation of the product compositions, from the dehydration of 3-methyl-2-butanol and 2-methyl-2-butanol from their equilibrium values at a catalyst composition of P/B equal to 1.0.

Although no complete and unambiguous proof for such an interpretation of the present results can be offered at this time, the conclusions appear to be both reasonable and consistent with the data available. Additional work is required to provide the necessary support. However, the present data does provide further information on the catalytic properties of boron phosphate and its relationship to other catalysts.

ACKNOWLEDGMENT

The financial support of the National Research Council of Canada is gratefully acknowledged.

REFERENCES

1. Noller, H., and Kladnig, W., *Catal. Rev. Sci. Eng.* **13**, 149 (1976).
2. Pines, H., and Haag, W. O., *J. Amer. Chem. Soc.* **83**, 2847 (1961).
3. Herling, J., and Pines, H., *Chem. Ind.* (*London*) 984 (1963).
4. Pines, H., and Manassen, J., *Advan. Catal.* **16**, 49 (1966).
5. Pillai, C. N., and Pines, H., *J. Amer. Chem. Soc.* **83**, 3274 (1963).
6. Lundeen, A. J., and Van Hoozer, W. R., *J. Org. Chem.* **32**, 3386 (1967).
7. Noller, H., Andreu, P., and Hunger, M., *Angew. Chem. Int. Edit.* (*Eng.*) **10**, 172 (1971).
8. Knözinger, H., *in* "The Chemistry of the Hydroxyl Groups" (S. Patai, Ed.), p. 641. Wiley–Interscience, New York, 1971.
9. Moffat, J. B., and Scott, L. G., *J. Catal.* **49**, 356 (1977); **45**, 310 (1976).
10. Moffat, J. B., and Chao, E., *J. Catal.* **46**, 151 (1977).
11. Moffat, J. B., and Riggs, A. S., *J. Catal.* **42**, 388 (1976); **28**, 157 (1973).
12. Moffat, J. B., and Neeleman, J. F., *J. Catal.* **39**, 419 (1975); **34**, 376 (1974).
13. Moffat, J. B., and Haleem, M. A., *Canad. J. Chem.* **45**, 1401 (1967).
14. Moffat, J. B., and Haleem, M. A., *Canad. J. Chem.* **43**, 3495 (1965).
15. Tada, A., Yoshida, M., and Hirai, M., *Nippon Kagaku Kaishi*, 1379, (1973).
16. Tada, A., and Mizushima, K., *Nippon Kagaku Kaishi*, 278 (1972).
17. Galeski, J. B., and Hightower, J. W., *Canad. J. Chem. Eng.* **48**, 151 (1970).
18. Goltz, H. L., and Moffat, J. B., *J. Catal.* **22**, 85 (1971).
19. Kilpatrick, J. E., Prosen, E. J., Pitzer, K. S., and Rossini, F. D., *J. Res. Nat. Bur. Stand. A* **36**, 559 (1946).
20. Carrizosa, I., and Munuera, G., *J. Catal.* **49**, 189 (1977).
21. Jacobs, P. A., Tielen, M., and Uytterhoeven, J. B., *J. Catal.* **50**, 98 (1977).
22. Jacobs, P. A., "Carboniogenic Activity of Zeolites," pp. 99–107, 131–135. Elsevier, Amsterdam, 1977.
23. Dautzenberg, D., and Knözinger, H., *J. Catal.* **33**, 142 (1974).
24. Bett, J. A. S., and Hall, W. K., *J. Catal.* **10**, 105 (1968).
25. Kibby, C. L., and Hall, W. K., *J. Catal.* **29**, 144 (1973).
26. K. Thomke, *J. Catal.* **44**, 339 (1976).
27. Knözinger, H., Bühl, H., and Kochloefl, K., *J. Catal.* **24**, 57 (1972).
28. Thomke, K., and Noller, H., *in* "Proceedings of the Fifth International Congress on Catalysis, Miami, 1972," p. 1183. North Holland, Amsterdam, 1973.
29. Bethell, D., and Gold, V., *in* "Carbonium Ions, An Introduction," p. 160. Academic Press, New York, 1967.