

A Relation Between the Product Distribution from the Dehydration of Dimethylbutan-2-ols and Catalytic Acidity

By SHANTAPPA S. JEWUR and JOHN B. MOFFAT

(Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L3G1)

Summary In the dehydration of 3,3-dimethyl- and 2,3-dimethyl-butan-2-ol, the formation of Hofmann alkanes (but-1-enes) is favoured by boron phosphate catalysts of relatively high surface acid concentrations, while those catalysts with lower acid concentrations promote the production of Saytzeff alkenes (but-2-enes); the activity and selectivity can be related to catalyst composition and surface acidity, and two simultaneously operative mechanisms, whose importance varies with catalyst composition, are tentatively proposed.

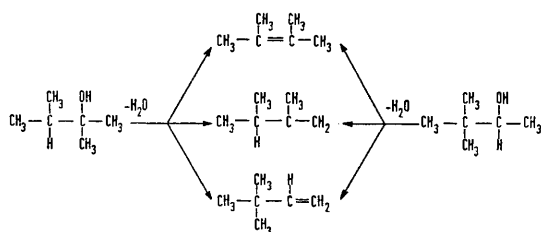
It is well known that the amount of a given alcohol that is catalytically converted into its dehydration products is related to the surface acidity of the catalyst involved.¹ Both Hofmann and Saytzeff alkenes are known to be produced from aliphatic alcohols containing more than three carbon atoms. However, the product distribution from the dehydration of a particular alcohol is a function of the catalyst employed.^{2,3} The dehydration of an alcohol may therefore proceed through different mechanisms on different catalysts. Further, different mechanisms may operate simultaneously during the production of the various alkenes from the dehydration of an alcohol on a

given catalyst. Several attempts have been made to determine the factors which are responsible for the formation of various surface intermediates during dehydrations catalysed by solid catalysts.^{3,4} Unfortunately, relatively little is known about the influence of surface acidity on either the mechanism or product distribution in the dehydration of alcohols.

We report here the results of experiments which show the importance of the acidity of boron phosphate catalysts on their activity and selectivity in the dehydration of 2,3-dimethyl- and 3,3-dimethyl-butan-2-ol. As will be seen, these are particularly appropriate molecules for probing the surface of an acidic catalyst. As far as we are aware only one study of the catalytic decomposition of these alcohols has been reported.⁵

The dehydrations of 2,3-dimethyl- and 3,3-dimethyl-butan-2-ol were studied at 150 °C, on both stoichiometric and non-stoichiometric boron phosphate catalysts with P/B molar ratios ranging from 0.4 to 1.4, in a microcatalytic pulse reactor with a constant reciprocal space velocity of 140 mol⁻¹ g min. The acidities of the various catalyst samples were estimated by measuring the quantity of ammonia irreversibly chemisorbed at room temperature.

Both the alcohols produced 2,3-dimethylbut-2-ene (2-3-2), 2,3-dimethylbut-1-ene (2-3-1), and 3,3-dimethylbut-1-ene (3-3-1).



In Figures 1 and 2, the product distribution, total mol of alkenes formed, and the molecules of ammonia chemisorbed per unit surface area are plotted as a function of P/B. The overall dehydration activity (mol of alkenes/m²) is found to follow the acidity pattern of the catalysts, that is, the greater the acidity, the higher the dehydration activity. Formation of Hofmann alkenes, *viz.*, 3-3-1 and 2-3-1, is maximum on the catalysts with a smaller number of acid sites whereas the concentration of the Saytzeff alkene, *viz.*, 2-3-2, is higher on the boron phosphates having greater acid site densities. Further, the 2-3-2 alkene is the major product of dehydration of both the dimethylbutanols on boron phosphate (Figures 1 and 2). In contrast, on

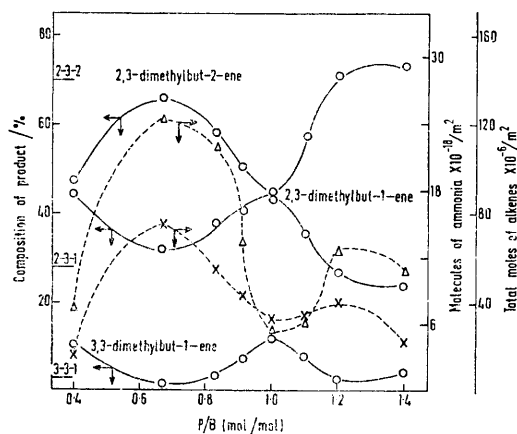


FIGURE 1. Correlation between the activity (---×---), product distribution (—○—), and the acidity (---△---) in the dehydration of 3,3-dimethylbutan-2-ol on boron phosphate catalysts (2-3-2, 2-3-1, and 3-3-1: equil. concns. of the alkenes).

alumina, in the presence of 10% w/w of piperidine, Pillai and Pines⁵ observed that 3-3-1 and 2-3-1 are the major products from the dehydration of 3,3-dimethyl- and 2,3-dimethylbutan-2-ol, respectively.

Since, in the present case, the catalytic activity is observed to be directly related to the acidity of the surface, it appears that the carbonium ion (E1) mechanism is

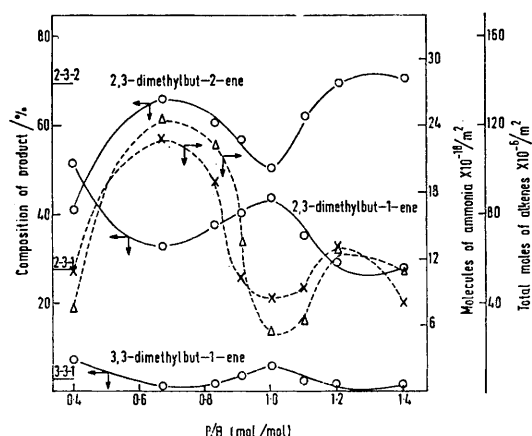


FIGURE 2. Correlation between the activity (---×---), product distribution (—○—), and the acidity (---△---) in the dehydration of 2,3-dimethylbutan-2-ol on boron phosphate catalysts (2-3-2, 2-3-1, and 3-3-1: equil. concns. of the alkenes).

operative over boron phosphate catalysts. This does not, however, preclude the existence of other mechanisms. Indeed, the observation of an inverse relationship between the concentrations of the Hofmann alkenes and the surface acidity of the catalysts suggests that another, probably secondary, mechanism is involved. Tentatively, we suggest that the Hofmann alkenes are formed through a concerted E2 mechanism.

A comparison of the graphs showing the total mol of alkenes formed from both the alcohols (Figures 1 and 2) indicates that 2,3-dimethylbutan-2-ol is twice as reactive as 3,3-dimethylbutan-2-ol. The higher reactivity of the former may be due to the presence of the methyl group at the α -carbon atom. This may facilitate the C—OH cleavage by virtue of the positive inductive effect associated with the methyl group. It is well known that tertiary alcohols are more reactive than secondary alcohols on acidic oxides.⁶ Further, the sensitivity of the extent of dehydration of the two alcohols to the α - or β -position of the second methyl group provides supportive evidence for the primary role of an E1 carbonium ion mechanism on boron phosphate.

Although conclusive evidence for the particular mechanisms operative in the dehydration of alcohols on acidic catalysts is not yet available, we believe that the present observations demonstrate the dependence of both activity and selectivity on surface acidity, the existence of two dominating mechanisms, probably an E1 carbonium ion and an E2 concerted mechanism, and the manner in which the relative importance of these two processes changes with the catalyst composition.

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