

## MECHANISM OF THE DEHYDRATION OF 1-BUTANOL OVER ZEOLITES

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The product distribution from the dehydration of 1-butanol over zeolites (13X, 4A, ZNa) has been investigated to gain insight of the reaction mechanism. The formation of 2-alkenes (*cis*-2-butene and *trans*-2-butene) in the absence of isomerization reactions during the catalytic dehydration of 1-butanol over zeolites is unambiguous evidence in favour of a positively charged intermediate, indicating that reaction proceeds *via* a E1 type of mechanism. Experimental data also showed the preferential formation of *cis*-2-butene over that of *trans*-2-butene. The predominance of E1 type mechanism increases with increasing temperature.

The study of product distribution of alkenes from the elimination reactions of organic compounds of the forms  $R_1-CH_2-CHXR_2$  is very helpful in shedding light on the reaction mechanism. Noller and coworkers<sup>1,2</sup> have given extensive reviews on elimination reactions over polar catalysts, including a section on the elucidation of reaction mechanism by examination of the product distribution.

Previous work on the dehydration of 1-butanol<sup>3-7</sup>, except that of Pines and Haag<sup>7</sup>, has not resolved the isomeric alkene products. The dehydration of 1-butanol over alumina was studied at reaction temperatures<sup>7</sup> of 350 and 420°C. It was found that some catalysts gave almost pure 1-butene while others produced mixtures of alkenes, that is 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene. At 350°C, values of the ratio of *cis* to *trans* isomers were found between 0.9 and 2.3 which were above the equilibrium value of 0.6. The formation of *cis*-isomer is explained by the formation of an intermediate proton olefin complex. Knözinger and Buhl<sup>8</sup> have observed a high *cis* preference during the catalytic dehydration of 2-butanol over alumina. Many authors<sup>9,10</sup> have also reported *cis*-preference during the catalytic elimination of haloalkenes.

The product distribution of butenes from the dehydration of 1-butanol over zeolites (4A, 13X, and ZNa) has been studied so as to gain some insight into the reaction mechanism.

### EXPERIMENTAL

The dehydration of 1-butanol has been studied over Laporte 13X, 4A, and Norton Zeolon (ZNa) zeolites. The physical and chemical properties have been given in the previous paper<sup>11</sup>. The most acidic of the three zeolites is the ZNa mordenite which has a  $SiO_2/Al_2O_3$  ratio of 10. The value of this ratio drops to only 2 in the case of 4A.

The dehydration reactions were conducted in a continuous stirred gas-solid reactor, where the catalyst was housed in a spinning basket. Details of the reactor with associated equipment and product analysis have been reported in the first paper<sup>11</sup> and thesis<sup>12</sup>.

## RESULTS AND DISCUSSION

The principal products of the dehydration reaction are butenes and dibutyl ether. The butene distribution consists mainly of 1-butene, *cis*-2-butene, and *trans*-2-butene. For all the catalysts used in the present study, isobutene was never detected under all reaction conditions. The kinetic has been analysed and modelled in the first paper<sup>11</sup>. The results and discussion presented here relate the production distribution and mechanism of the reaction.

*Effect of Partial Pressure*

Typical results are shown in Figs 1–3. The percentages of all the components were found to be independent of the partial pressure of 1-butanol. The same behaviour was observed at all reaction temperatures. This suggests that the rates of formation of alkenes are of the same order with respect to 1-butanol partial pressure. Jewur and Moffat<sup>12</sup> have found that the percentage concentration of 1-butene, *trans*-2-butene, and *cis*-2-butene remained the same for all the space times used during the catalytic dehydration of 2-butanol.

The formation of 1-butene over 13X zeolite predominates at all alcohol partial pressures. This indicates that 13X zeolite favours the formation of 1-butene, while

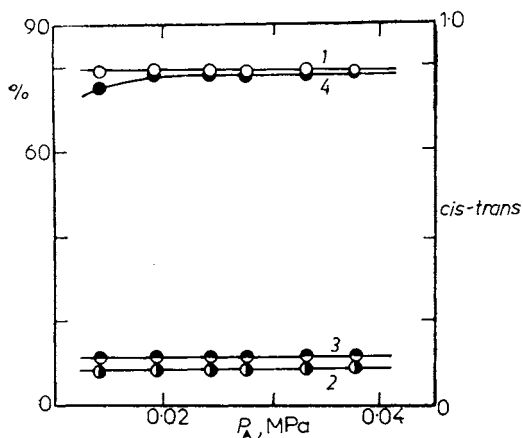


FIG. 1

The effect of the partial pressure of 1-butanol on the percentage distribution of butenes using zeolite 13X at 252°C. 1 1-Butene, 2 *cis*-2-butene, 3 *trans*-2-butene, 4 *cis/trans* ratio

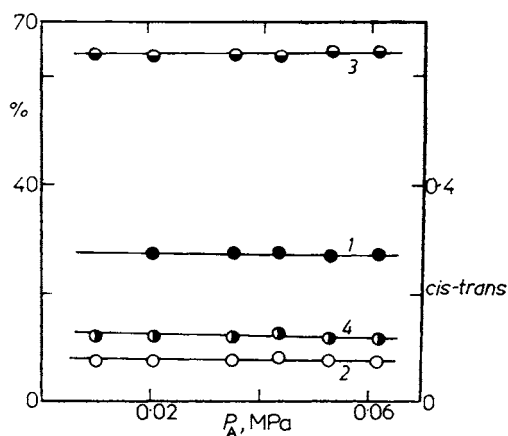


FIG. 2

The effect of the partial pressure of 1-butanol on the percentage distribution of butenes using zeolite 4A at 297°C. 1 1-Butene, 2 *cis*-2-butene, 3 *trans*-2-butene, 4 *cis/trans* ratio

*trans*-2-butene is favoured over zeolite 4A at all 1-butanol partial pressures. For the ZNa zeolite, at 235°C, the production of *trans*-2-butene, predominates at all partial pressures. However, at higher temperatures, the percentage of 1-butene was slightly higher than that of *trans*-2-butene at all alcohol partial pressures.

### Effect of Temperature

Figs 4–6 show the effect of reaction temperature on the distribution of butenes for the zeolites 13X, 4A, and ZNa, respectively. For 13X zeolite, 1-butene isomer was the main product in the temperature range studied. However, the percentages of other isomers increase slightly with increasing temperature. This is an indication either of the reaction mechanism shifting towards E1 type or that a Wagner–Meerwein rearrangement takes place relatively faster. This will be discussed later.

For zeolite 4A, *trans*-2-butene predominates at all temperatures. Its percentage increases with increasing reaction temperature, while the percentage of 1-butene falls sharply with increasing reaction temperature. The fraction of *cis*-2-butene also increases with increasing reaction temperature. Increasing production of 2-butenes with increasing reaction temperature is considered to be an important criterion for a

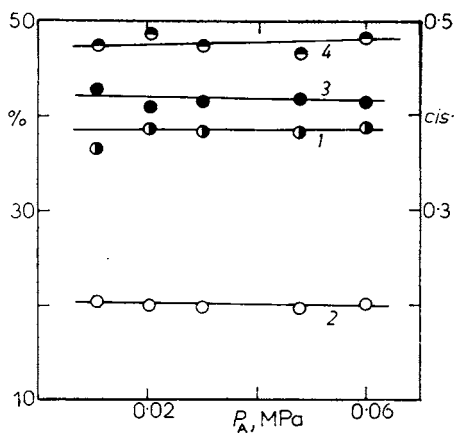


FIG. 3

The effect of the partial pressure of 1-butanol on the percentage distribution of butenes using zeolite ZNa at 235°C. 1 1-Butene, 2 *cis*-2-butene, 3 *trans*-2-butene, 4 *cis/trans* ratio

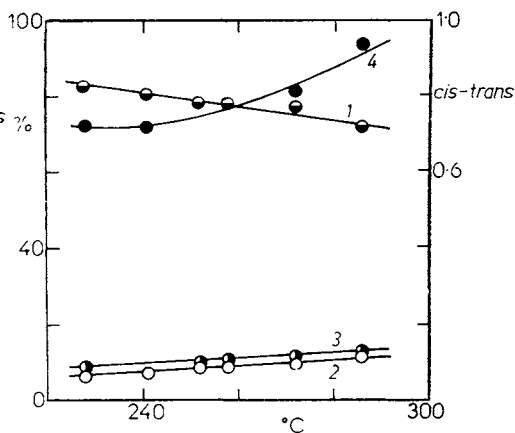


FIG. 4

The effect of the reaction temperature on the percentage distribution of butenes for the zeolite 13X. 1 1-Butene, 2 *cis*-2-butene, 3 *trans*-2-butene, 4 *cis/trans* ratio

shift of reaction mechanism from E2 to E1. This assumes that the dehydration reaction is taking place according to E2 type mechanism at lower temperature.

The formation of 1-butene over ZNa zeolite increases slightly from 37% at 235°C to 41% at 300°C, whereas the percentage of *trans*-2-butene falls slightly from 42% at 235°C to 33% at 300°C. The total percentage of 2-butenes slightly decreases from 63% at 235°C to 59% at 300°C. This probably indicates either one of the following: a) Increasing reaction temperature does not change the mechanism of the reaction over zeolite HNa. b) The catalyst selectivity towards the formation of 1-butene increases with increasing reaction temperature.

Two effects which may explain the former possibility are the effects of reaction temperature or acidic sites on reaction mechanism. Increasing reaction temperature or acidic strength shifts the reaction mechanism towards E1 type. The number of acid sites, especially the strongest ones, may be deactivated by the increasing temperature. If this happens, the reaction mechanism shifts towards E2 type. These two effects on the changing of reaction mechanism probably balance each other, hence the reaction mechanism on ZNa zeolite becomes independent of reaction temperature.

The ratio of *cis*-2-butene to *trans*-2-butene increases with increasing reaction temperature for all the catalysts. This suggests that all the catalysts are more selective towards the formation of the *cis*-isomer.

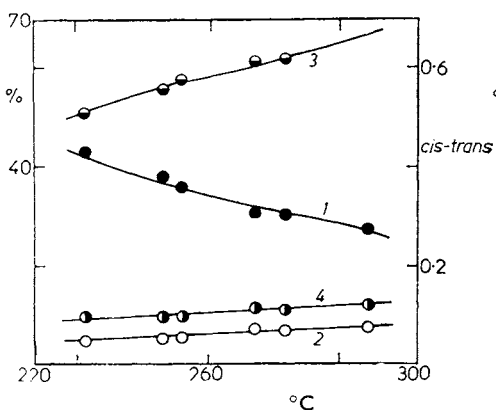


FIG. 5

The effect of the reaction temperature on the percentage distribution of butenes for the zeolite 4A. 1 1-Butene, 2 *cis*-2-butene, 3 *trans*-2-butene, 4 *cis/trans* ratio

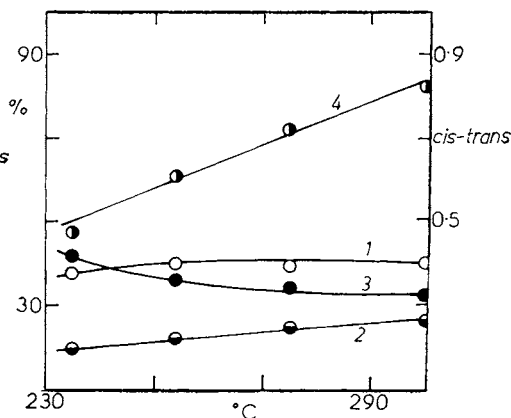
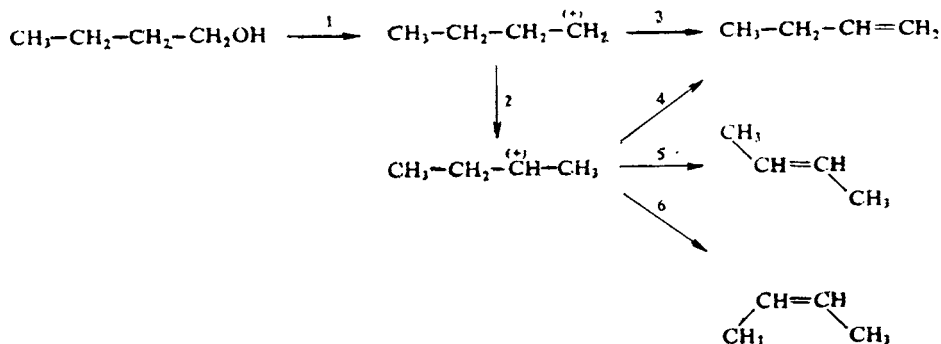


FIG. 6

The effect of the reaction temperature on the percentage distribution of butene for the zeolite ZNa. 1 1-Butene, 2 *cis*-2-butene, 3 *trans*-2-butene, 4 *cis/trans* ratio

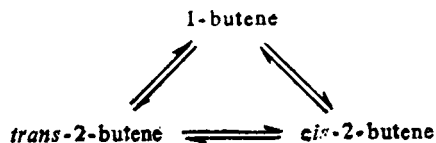
### Mechanism

The only mechanism that can explain the formation of the isomeric butenes from the dehydration reaction is the E1 type mechanism. E2 like mechanism leads to the formation of 1-butene. However, E2 type mechanism followed by secondary isomerization reactions of 1-butene can also account for the formation of other isomeric products. The production of 2-alkenes (*cis* and *trans*) in the absence of secondary isomerization reactions strongly suggests a dehydration reaction proceeding according to E1 mechanism.



SCHEME 1

The proposed dehydration reaction scheme according to E1 mechanism is represented as Scheme 1, while Scheme 2 shows the secondary isomerization reactions. From the suggested reaction scheme, 1-butyl carbonium ion undergoes the Wagner–Meerwein rearrangement to form the 2-butyl carbonium ion. 1-Butene can be produced from both 1- and 2-butyl carbonium ions, while the 2-alkenes can only be produced from 2-butyl carbonium ion. This, therefore, suggests that the production



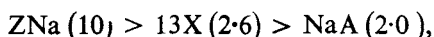
SCHEME 2

of 2-alkenes, both *cis* and *trans*, depends on the Wagner–Meerwein rearrangement reaction. The above reaction scheme cannot lead to the production of isobutene. If isobutene is produced, it must be from the skeletal isomerization reactions of the butenes. The most probable isomers are the 2-butenes. The formation of isobutene

requires the migration of a methyl group from carbon 2 to carbon 3 or *vice versa*. Therefore, the formation of isobutene needs further readsorption of 2-butenes. However, the 2-butenes are weakly adsorbed on active sites of the catalyst compared with butanol<sup>12-16</sup>. Therefore, the readsorption of 2-butenes is highly unlikely, because 2-butenes cannot compete with 1-butanol which is strongly adsorbed and present in much higher concentrations. Secondly, the absence of isobutene may be due to diffusional limitations because the bulky groups are attached to the same carbon atom. This, however, cannot explain its absence on zeolite 13X which has large cavities. The non-absence of isobutene is an important criterion which indicates that isomerization reactions did not occur. 2-Butenes are therefore produced independently through the same intermediate and 1-butene is probably formed through three different routes or intermediates (1-butyl carbonium, 2-butyl carbonium and E2 type mechanism).

This conclusion appears to contradict that of Pines and Haag<sup>7</sup>, who reported the presence of secondary isomerization reactions at their working temperatures. However, the present study was conducted at much lower reaction temperatures. The absence of skeletal isomerization reactions at low temperature may not be surprising, because isomerization reactions require temperatures higher than that of the dehydration reactions.

There is no doubt that the type of catalyst used affects the products distribution. Two physico-chemical properties are responsible for the different product distribution. There are pore geometry and the presence of acidic and basic sites. It is well known that both acidic and basic sites are necessary for the catalytic dehydration of alcohol to olefin irrespective of the type of mechanism the reaction follows. The order of acidic strength of the zeolites used in the present study is



where the number within the brackets indicates the ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$ . This ratio indicates that acidic sites are predominant on these zeolites. E1 type mechanism, therefore, would be expected for the elimination reactions over these zeolites.

For zeolites 4A and ZNa, the E1 mechanism is preferred under all reaction temperatures. This is shown by the total percentage of 2-butenes which is equal to or above 55% of the butene production. For the Zeolite 4A, increasing temperature further increases this percentage, indicating that increasing temperature further shifts the mechanism towards E1 type. A similar change in mechanism for E2 to E1 type has been reported by Noller and coworkers<sup>2</sup> and Knözinger and Scheglila<sup>13</sup> for the elimination reactions of haloalkanes and 2-butanol.

The production distribution over zeolite 13X shows that 1-butene is highly favoured. This may be explained by the following (Scheme 1):

a) Reaction step 3 is very fast and only a small amount of 1-butyl carbonium ion undergoes Wagner–Meerwein rearrangement (reaction step 2) producing small amounts of 2-butenes (*cis* and *trans*). The Wagner–Meerwein rearrangement probably requires a vacant site which might lead to formation of some 2-butyl carbonium ion, because the active sites are nearly saturated by the reactant. This is supported by the low reaction order with respect to 1-butanol concentration obtained<sup>11</sup>.

b) If the Wagner–Meerwein rearrangement, reaction step 2, does occur rapidly, because 1-butyl carbonium ion is less stable, as suggested by Kladnig and Noller<sup>9</sup> than reaction step 4, must be very fast compared with steps 5 and 6, before zeolite 13X could become highly selective to the formation of 1-butene.

c) The preferential production of 1-butene on zeolite 13X may be due to E2 mechanism predominance. That is most of the 1-butene is produced according to E2 mechanism, while E1 mechanism contributes much less towards the formation of 1-butene. However, the fact that 2-butenes (*cis* and *trans*) are produced in the absence of isomerization reactions suggests strongly that the dehydration reaction probably proceeds through an ionic mechanism.

The dehydration of 1-butanol proceeds according to an ionic mechanism on NaA which has the lowest acidic strength. An increase in acidic strength in zeolites shifts the mechanism for the elimination reaction further towards E1 type. This is borne out in the case of ZNa which has the highest acidic strength. Therefore the dehydration of 1-butanol most probably proceeds according to E1 mechanism with preferential formation of 1-butene as the principal alkene product. Kladnig and Noller<sup>9</sup> have also observed that 1-butene predominates in the elimination of 1-chlorobutane over Linde 13X, but concluded that it was an indication of the E2 type mechanism. However, they failed to consider the fact that 1-butene can be produced through reaction step 4. The preferential formation of 1-butene from 1-halobutane has been observed on lithium salts<sup>1,10</sup>. Production of 2-butenes (*cis* and *trans*) from 1-halobutane was considered as an important indication of the elimination reaction proceeding through E1 mechanism. The argument is in agreement with that proposed here for the dehydration of 1-butanol. The above conclusion is consistent with the Hougen–Watson rate model based on dual site mechanism which has been shown in the earlier paper to correlate the kinetics of 1-butanol dehydration to butene over zeolites. Other oxide catalysts reported in the literature<sup>4,5,7</sup> support this dual acid-base site mechanism.

## CONCLUSIONS

The percentage distribution of butenes (1-butene, *cis*-2-butene, and *trans*-2-butene) was found to be practically independent of partial pressure of 1-butanol at a given reaction temperature. *cis*-Preference was observed on zeolite 13X and ZNa. The

dehydration of 1-butanol to butenes over the zeolites used was found to proceed through E1 mechanism, although E2 type mechanism cannot be precluded entirely for the case of zeolite 13X. The predominance of E1 type mechanism increases with increasing reaction temperature.

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