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# LETTERS TO THE EDITORS

## Comments on "Study of Interaction of Aliphatic Alcohols on $TiO_2$ II on the Mechanism of Dehydration on Anatase"

The results obtained for the dehydration of alcohols on anatase, reported by Carrizosa (*1*), suggest that the catalyst exhibits both the *syn* and *anti* modes of elimination depending on the conditions of dehydration.

The low 1-olefin/2-olefin ratio of 0.5 for 2-butanol over anatase and a high *cis–trans* ratio of 2.0, suggest that an *anti* mode of elimination over a fairly acidic-type catalyst is what is extant.

The generalization, viz., the selectivity for 1-olefin formation and *syn* elimination complementing each other, need not always be true. The studies (*2*) conducted over alumina and sodium-impregnated alumina samples, indicated an increased propensity for terminal olefin formation with increase in sodium content in the catalyst sample. The sodium impregnation increases the basicity of the sample, due to which the transition state shifts to a more E1CB-like one, abstracting preferentially a highly acidic hydrogen atom, while the mode of elimination just remained *anti*, as evidenced by almost identical product distribution in the case of pure and sodium-impregnated alumina samples with threo-3-methyl-2-pentanol.

While increase in basicity is borne out by enhanced terminal olefin formation, the *anti* mode of elimination is manifested in the high *cis–trans* ratio.

With 2-butanol, alumina gave a high ratio for *cis–trans*, (4.5), whereas *syn*-elimination thoria afforded a low ratio (1.0). During a *syn*-mode elimination from synperiplanar or synclinal conformation, the steric strain between the substituents become important, hence the transition state leading to *trans*-olefin is preferred.

The 1-olefin selectivity is decided by the surface acidity–basicity characteristics and not always by the *syn* mode of elimination. It is accidental that, with thoria, both the *syn* mode and 1-olefin predominance are observed.

The olefin selectivity is decided by the basicity of the catalyst and the mobility (acidity) of the hydrogen atom abstracted for elimination to occur. Dehydration studies over thoria with benzylmethylcarbinol—where the methylene (secondary) hydrogens are made more acidic by phenyl substitution compared to methyl hydrogens—gave a high selectivity for 2-olefin formation.

In homogeneous elimination studies (*3*) with threo-1-halo-1,2-diphenyl-2-p-totylsulfonyl ethane, a change of geometric orientation from complete *syn* to *anti* has been observed upon variation in base strength from high to low, while the erythro diastereomer, irrespective of base strength, eliminated by *anti* mode. The extension of such a concept, without substantial evidence, to heterogeneously catalyzed elimination reactions may not be valid.

The different modes of elimination could be a result of the porous nature of the catalyst. When a highly porous catalyst is used, elimination proceeds by an *anti*

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mode from energetically favored antiperiplanar conformation.

When the catalyst is less porous, then the reaction has to take place, on the plain surface, by necessarily a *syn* mode of elimination from the strained synperiplanar or synclinal conformation. To force the molecule into this conformation, a higher energy is required, which is exemplified by the high temperature needed for these reactions.

It could be due as well to the size of $O^{2-}$ ion, which acts as basic site, which facilitates the *anti* mode of elimination even in the absence of porosity as suggested by Hall *et al.* (*4*). If such a disposition, of exposed cations and large $O^{2-}$ ions covering adjacent lattice positions, is available in anatase, such an *anti* mode of elimination would be made possible in spite of the lack of porous nature.

These reactions over anatase taking place at relatively low temperatures, the high *cis–trans* ratio and low 1-olefin-2-olefin ratio seem to have been due to operation of an *anti* mode of elimination on a fairly acidic catalyst.

The decreased 1-olefin formation at higher temperatures could be due to a more favored rehydration of the surface which might increase the acidity. This, in turn, shifts the $E_2$-transition state to a more $E_1$-like one and hence the higher selectivity for 2-olefin formation at high temperatures.

## REFERENCES

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S. Siddhan

*Analytical Division*
*Regional Research Laboratory*
*Hyderabad 500 009 [A.P]*
*India*

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