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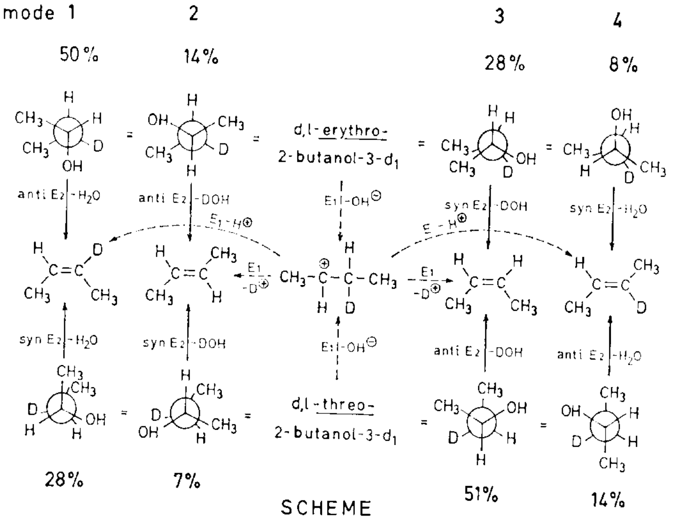
On the Transition State of Dehydration

Dehydrations as well as other elimination reactions exhibit two striking phenomena: (i) preference of the thermodynamically disfavored *cis*-olefins, and (ii) occurrence of anti-elimination.

A few years ago, Knözinger, Bühl, and Kochloefl (*1*) proposed an explanation assuming that the group HO–C–C–H is not perpendicular to the surface in the transition state, but inclined so that bulky groups are directed away from the surface. With little strain, a simultaneous contact of OH and β-H is possible even with plane surfaces. This proposal was made on the basis of the existing results about *cis*-preference and the possibility of an anti-mechanism, without being based upon more direct experimental evidence.

In our studies on the stereochemistry of dehydration (for the experimental procedure, see Thomke and Noller (*2*)), we used *d,l*-erythro-(threo-)-2-butanol-3-d_1 (erythro, threo). The initial conformers and the modes for the formation of 2-butenes are represented in the following scheme:



SCHEME

Four 2-butene species can be formed (i.e., *cis*-2-butene-2-d_0, *cis*-2-butene-2-d_1, *trans*-2-butene-2-d_0, and *trans*-2-butene-2-d_1), which indicate the elimination mode and also the initial conformer. Over $MgAl_2O_4$ (for the preparation, see Vinek and Ebel (*3*)), the results in Table 1 were obtained.

As described recently (*2*, *4*) the percentage of occurrence of the four elimination modes for 2-butene formation was calculated taking into account the kinetic isotope effect. The data are indicated in the scheme. They correspond to those which should be obtained if there was no kinetic isotope effect.

It is clearly seen that those conformers which have their methyl groups on the same side of the carbon skeleton (modes 1 and 3) are considerably favored in comparison to those having their methyl groups on opposite sites (modes 2 and 4). This result is best explained by assuming the inclination proposed by Knözinger *et al.* (*1*). The steric hindrance due to the methyl groups is very similar, perhaps equal for erythro and threo. In both cases, the favorable conformers contribute about 80% to the total production of 2-butene, i.e., about 80% of 2-butene is the *cis*-isomer. About the same ratio is even found for either anti-elimination or syn-elimination.

Whereas in liquid phase almost only anti-elimination has been found, in contact eliminations the syn-mechanism has a rather high percentage, in this case, roughly 35%. This has probably also to do with steric hindrance. In the inclined position, some strain is necessary for a simultaneous contact, with the surface, of OH and H of the staggered conformer. This strain reduces somewhat the advantages of the staggered conformer and anti-elimination. Therefore the eclipsed conformers (3 and 4 for erythro, 1 and 2 for threo) are less disfavored than in the liquid phase. Conformer 3 of erythro is even more favorable for the reaction than the staggered conformer 2 and, similarly, conformer 1 of threo is more favorable than 4.

The inclination is also probable from a theoretical point of view. Both the bonding and the nonbonding orbitals at O of the OH group are directed with angles, say, between 90 and 108°. The interaction, and therefore the catalytic effect, is strongest and the strain least when the bond angles are of this magnitude. Although perpendicular adsorption is not strictly excluded, it is one of numerous possibilities and probably not the best one, i.e., the one with smallest strain.

With other spinels (Zn, Co, Ni) and further with γ-alumina a similar population of the four elimination modes was found.

TABLE 1

Product Distribution and Percentage of Deuterated Molecules

	Temperature (°C)	1-Butene	*trans*-2-Butene	*cis*-2-Butene
Erythro	320	32 (100)	13 (49)	55 (76)
Threo	320	33 (99)	16 (77)	51 (50)

REFERENCES

1. Knözinger, H., Bühl, H., and Kochloefl, K., *J. Cat.* **24**, 57 (1972).
2. Thomke, K., and Noller, H., *Proc. Int. Congr. Catal.*, 5th, Vol. 3, paper 84, p. 1183.
3. Vinek, H., and Ebel, M., *Z. Physik. Chem. NF*, **99**, 145 (1976).
4. Ruthner, H., and Noller, H., *J. Catal.* **38**, 264 (1975).

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