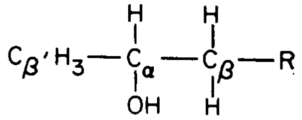
JOURNAL OF CATALYSIS 33, 142–144 (1974)

Influence of Steric and Inductive Effects on Product Distributions in the Dehydration of Secondary Alcohols on Alumina*

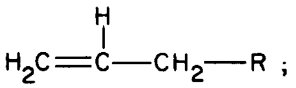
At sufficiently low temperatures ($<250°C$) the dehydration of aliphatic alcohols proceeds through an E 2-like reaction intermediate on alumina (*1–4*). The hydroxyl group and β-hydrogen are abstracted predominantly from an antiperiplanar position (*1–3, 5*). A model mechanism has recently been proposed to explain these observations (*6*). The alcohol molecule is assumed to be adsorbed via the hydroxyl group and to retain some vibrational and rotational freedom relative to the surface which enables the β-hydrogens in an antiperiplanar position relative to the OH-group to approach a basic surface site. The primary product distributions are determined by inductive and steric effects of alkyl groups at C_α and C_β according to this model. The generally high *cis*-preference in particular is explained by steric hindrance between the reacting molecule and the catalyst surface, which renders the approach of the β-hydrogens to a basic site more probable and thus more frequent for conformations with the most bulky substituents at C_α and C_β in a synclinal position relative to each other.

The present contribution is devoted to test the substituent effects on product distributions in more detail. A series of secondary alcohols of the general structure

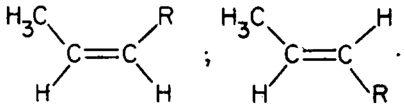


$$C_{\beta'}H_3-\underset{OH}{\overset{H}{C_\alpha}}-\underset{H}{\overset{H}{C_\beta}}-R$$

has been chosen with the substituents R being Me, Et, *n*-Pr, *i*-Pr and *t*-Bu. The product olefins are the respective 1-olefins and *cis*- and *trans*-2-olefins of the general structures:



$$H_2C=\overset{H}{C}-CH_2-R\ ;$$



The catalyst was a high-purity η-Al_2O_3 which was prepared from aluminum isopropoxide by hydrolysis with distilled water and thermal treatment of the resulting hydroxide at 700°C in air. It had a BET surface area of 180 m^2/g. The particle size fraction of 0.2–0.3 mm was used. The reaction was carried out in a conventional differential flow type reactor using helium as a carrier gas. The details of the apparatus and the procedures are described by Hajek and Kochloefl (*7*). Transport phenomena did not affect the conversions and product distributions. Experimental conditions were always chosen such that conversions were less than 15% (usually between 1 and 10%) and secondary reactions did not influence the primary product distributions. Analyses were carried out by gas chromatography using mostly a benzylcyanide/$AgNO_3$ on Chromosorb W column (length 3 m, diameter 0.4 cm) in combination with a dimethylsulfolane on Chromosorb W column (length 4 m, diameter 0.4 cm) at 20–40°C (depending on olefin mixture) and 50 cc/min helium carrier gas for the separation of the isomeric olefins. The mean errors on the conversion data were approximately 6–7%. Since the reactions

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* Part XVII of the series "Dehydration of alcohols on alumina."

were zero order under the conditions used, the number of moles of a given product formed at a given space velocity is a good measure of the respective rate constant and relative product concentrations are defined as selectivities as follows:

$$S_{21} = \frac{\text{concn of product 2-olefins}}{\text{concn of product 1-olefins}}$$

and

$$S_{ct} = \frac{\text{concn of } cis\text{-2-olefin}}{\text{concn of } trans\text{-2-olefin}}.$$

The results obtained at 210°C are summarized in Table 1. Both selectivities decrease with increasing volume of the substituent R in the sequence

Me > Et > *n*-Pr > *i*-Pr > *t*-Bu.

The logarithm of the selectivities S_{21} can be linearly correlated with Taft's inductive constant σ^* (*8*) as shown in Fig. 1. The correlation coefficient is 0.996, whereas no linear correlation can be obtained with the steric constants E_s (*8*). The inductive effect of the substituents R will only alter the reactivity of the β-hydrogens without influencing the reactivity of the β'-hydrogens. The S_{21}-values therefore decrease in the observed sequence because of the reduced rate of formation of the 2-olefins with increasing inductive power of the substituent R. The S_{21}-selectivity is predominantly governed by inductive effects, the rupture of C_β–H bonds being involved in the rate determining step in accordance with observed kinetic deuterium-isotope effects (*4*).

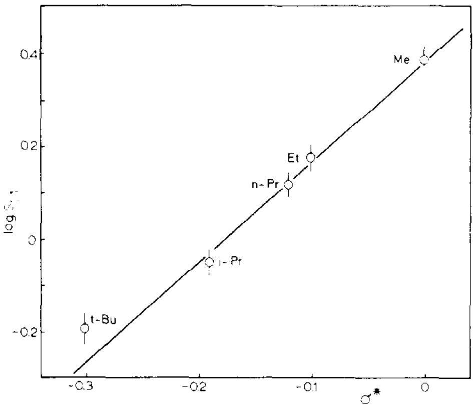


FIG. 1. Correlation of selectivity S_{21} with Taft's inductive constants, $T = 210°C$; $\rho = +2.2$.

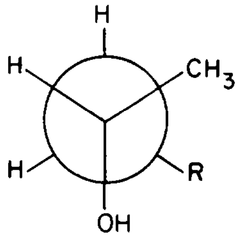
The selectivities S_{ct} are in all cases higher than unity, whereas the thermodynamic equilibrium values are around 0.5–0.6. This preferred formation of the *cis*-olefin may be explained by the assumption of steric interactions between bulky substituents in the reactant molecules and the catalyst surface. This view was put forward previously (*6*) within the scope of a model mechanism. The adsorbed alcohol molecules will exist in two conformations with respect to the methyl group at C_α and the variable substituent R at C_β, i.e., antiperiplanar and synclinal conformations will be present. The former conformation, which would lead to the *trans*-2-olefin on anti-elimination, is most probably thermodynamically preferred due to lower intramolecular steric strain. According to the model mechanism previously proposed (*6*), however, the reaction probability of the synclinal conformations is expected to be higher than that of the antiperiplanar conformation. The approach between the β-hydrogen in the antiperiplanar position relative to the OH-group and a basic site is least hindered during a

TABLE 1

SELECTIVITIES IN DEHYDRATION OF SECONDARY ALCOHOLS ON η-Al_2O_3 AT 210°C

Substituent R	σ^*	E_s	S_{21}	S_{ct}
Me	0	0	2.4 ± 0.16	5.9 ± 0.3
Et	−0.1	−0.07	1.5 ± 0.1	5.5 ± 0.35
n-Pr	−0.12	−0.36	1.3 ± 0.1	5.2 ± 0.35
i-Pr	−0.19	−0.47	0.96 ± 0.07	4.7 ± 0.3
t-Bu	−0.30	−1.54	0.64 ± 0.05	2.1 ± 0.2

suitable vibration phase relative to the surface of the synclincal conformation:



Thus, reaction will occur most probably and hence most frequently for synclinal conformations during the appropriate phase of a vibration (or rotation) relative to the surface of a potentially reactive surface species. This increased reaction probability may overcompensate the lower surface concentration of the synclinal compared to the antiperiplanar conformation and thus cause the high S_{ct}-values (*cis*-preference). Due to the intramolecular steric strain between the methyl group and substituent R, one would expect a decrease of the relative concentrations of the synclinal conformations with increasing volume of R and consequently a decrease in the S_{ct}-values, which is in fact observed (see Table 1). The logarithms of the S_{ct}-selectivities can be linearly correlated with Taft's steric constants E_s (*8*) as shown in Fig. 2 (correlation coefficient 0.994). A linear correlation with the inductive constants σ^* on the other hand is not obtained.

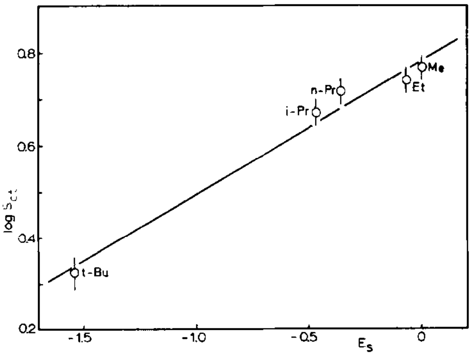


FIG. 2. Correlation of selectivity S_{ct} with Taft's steric constants, $T = 210°C$; $\delta = +0.3$.

ACKNOWLEDGMENT

Financial support by the Fonds der Chemischen Industrie and by the Fritz-ter-Meer-Stiftung is kindly acknowledged.

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Received June 29, 1973; revised October 9, 1973