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EFFECTS OF ALKALI-CATION EXCHANGE ON THE STEREOCHEMISTRY OF β-ELIMINATION OF ALKYL HALIDES OVER SILICA GEL

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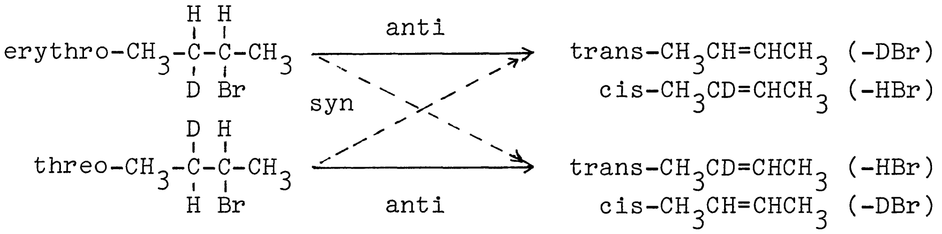
Dehydrobromination of 2-bromobutane and 2,3-dibromobutane proceeded mainly by anti mode over K- and Cs-exchanged silica gel, but syn mode over silica and Li-silica. Upon re-exchange of K and Cs with proton the steric course returned to syn mode. Role of acid-base properties of solid surface and substrate in controlling the steric course was suggested.

Several studies have been reported on the stereochemistry of elimination reaction (syn or anti mode), particularly of dehydration of alcohols, catalyzed by solid catalysts.[1-6] However, the problem what is the essential factor controlling the steric course of reaction still remains unsolved, owing to the fact that the structure of catalyst surface is not known in the dimension of a substrate molecule. Thus, some investigators speculated the role of steric factors such as geometry of surface sites,[1,6] while some suggested the importance of acid-base properties of catalyst or substrate.[2,4,5] In order to determine whether the observed stereochemistry is controlled by the steric factors or the chemical (acid-base) ones, we have studied the effects of the variation of one factor keeping the other factors as constant as possible.

In this letter we report novel effects of alkali-cation exchange on the stereochemistry of β-elimination over silica gel. Reaction studied is dehydrobromination of 2-bromobutane and 2,3-dibromobutane at 100-160°C. Alkali-exchanged silica gel (abbreviated hereafter as K-SiO_2, etc.) was prepared by soaking silica gel (from hydrolysis of tetraethoxysilane) three times in aqueous solution (N/20) of alkali chloride and carbonate (ca. 2:1) with vigorous shaking for several hours each time at room temperature. Initial pH of the solution was adjusted every time to 8.0 or 10.0 by the addition of small amount of hydrochloric acid. They were washed and dried at 110°C and preheated in a reactor at 300°C for 1 hr in a stream of dry helium or hydrogen. The alkali contents were determined by flame photometry. A pulse technique utilized in this work and the methods of products analyses and of preparation of reagents have been described elsewhere.[5)]

Table 1 shows the contents of d_1 species in 2-butenes formed over SiO_2 and K-SiO_2 from erythro-2-bromobutane-3-d_1 which contains 17% of threo isomer and 6% of d_0 species. No isomerization of products took place under the reaction conditions.

Higher d_1 content in cis-2-butene than in trans-2-butene indicates anti elimination and the opposite relative d_1 content means syn elimination (cf. the scheme below).



Results in Table 1 show that the favored steric course changed from syn to anti mode by the K-exchange of silica surface. Further, the steric course returned to syn mode, when most of K^+ ions in K-SiO_2 were removed by repeated washing with aqueous HCl solution of pH 4. Variation in the butene composition due to the deuterium isotope effects$^{5)}$ was in accord with this change in the stereochemistry. In the last column of Table 1, the stereoselectivity estimated from the d_1 content and the butene composition is presented, on the assumption that the stereoselectivity and the isotope effects are identical for trans- and cis-2-butene formation. This assumption held fairly well in the cases of SiO_2 and KOH-treated SiO_2.$^{5)}$ Since the surface structure of silica gel itself remained almost unchanged in the exchange procedure as indicated by little change in the surface area (especially in the K→H treatment), it may be stated that the steric course of reaction changed nearly reversibly between anti and syn mode by the exchange with K^+ ion of a few

Table 1 Variation of Stereochemistry of Dehydrobromination of 2-Bromobutane over Silica Gel by Alkali-Exchange

Catalyst	Amount of K (mg-ion/g)	Surface area (m^2/g)	Relative activity	d_1 content of 2-butene from 2-bromobutane-3-d_1^{a} trans	cis	Stereo-selectivity
SiO_2^{b}	0.0	425	1.0	76%	42%	syn 81%
K-SiO_2^{c}	0.12	400	3.3	47	70	anti 71
H-SiO_2^{d}	0.01	390	0.7	68	46	syn 70

Reaction temperature: 160°C

a) erythro isomer 77%, threo isomer 17% and d_0 species 6%.

b) SiO_2 was calcined at 800°C.

c) SiO_2 calcined at 800°C was treated with KCl-K_2CO_3 aq. solution (N/20, pH=8).

d) K-SiO_2 was decationized by washing with aq. HCl (pH=4).

Table 2 Stereochemistry of Dehydrobromination of 2-Bromobutane over Alkali-Exchanged Silica Gels

Alkali-SiO_2[a]	Amount of alkali (mg-ion/g)	Reaction temp. (°C)	Relative activity at 160°C	d_1 content of 2-butene from 2-bromobutane-3-d_1[b] 1-	trans	cis	Stereo-selectivity
Li	0.04	160	1.5	92%	67%	53%	syn 62%
Li	0.50	160	3.3	95	78	49	syn 76
Na	0.07	160	0.8	92	75	48	syn 74
Cs	0.08	160	1.0	-	38	74	anti 80
Cs	0.55	100	3.8	96	25	87	anti 100

a) SiO_2 was calcined at 500°C. b) See footnote (a) of Table 1.

per cent of surface silanol groups (total surface SiOH, ca. 4-5/100A^2).[7] Preferred anti elimination was also observed upon K-exchange of SiO_2 which was calcined at 1000°C prior to exchange and had surface area of only about 100 m^2/g.

Effect of cation species is further demonstrated by the results in Table 2. Syn elimination was favored over Li- and Na-SiO_2 and anti elimination over Cs-SiO_2. Re-exchange of Cs with proton returned the steric course to syn mode. Anti-selectivity was in the order of Cs > K > Na ~ Li. This trend did not change by the alkali content, while the activity more or less increased with the increasing alkali content. It is worthwhile to note that stereoselectivity of almost 100% was observed over solid surface (Cs, 100°C).

Dehydrobromination of meso- and dl-2,3-dibromobutane proceeded selectively (>90%) by anti mode over Cs-, K-, and even over Na-SiO_2. The selectivity was not determined over Li-SiO_2 because of its very small activity for this reaction.

Present results that the stereochemistry was controlled by the cation species may be explained on the basis of acid-base properties of catalyst and substrate as in the case of KOH-treated SiO_2.[5] The acid strength of cation increases with its electronegativity as Cs < K < Na < Li,[8] while the basicity of oxide ion coordinated with alkali cation is likely to decrease as OCs > OK > ONa > OLi. If one takes into account the proposed variation in the mechanism of β-elimination depending on acid-base strength,[9,10] it seems most likely that the elimination of H and Br from 2-bromobutane occurs nearly concertedly by anti mode over basic solids such as Cs- and K-SiO_2. Ordinary roughness of the surface of metal oxides has been suggested to satisfy geometrical requirements for anti elimination.[2,3] On the other hand, surface sites on weakly acidic Na- or Li-SiO_2 being insufficiently basic to abstract a β-proton, the proton may be abstracted by a releasing Br atom to form a HBr molecule (syn elimination). In accord with this idea, large poisoning effect of pyridine added to catalyst prior to the reaction was observed with Li-SiO_2, whereas pyridine little affected the activity of Cs-SiO_2. It has been reported that Cs- and K-zeolite are basic and Li-zeolite is acidic.[11)] Similar variation of stereochemistry with the basicity of attacking reagent has been reported for eliminations in the liquid phase.[12)] Opposite stereochemistry over Na-SiO_2 between 2,3-dibromobutane and 2-bromobutane may be ascribed to the much stronger acidity of β-proton of dihalides which favors concerted elimination.

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