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STEREOCHEMISTRY AND ISOTOPE EFFECT IN THE DEHYDROBROMINATION OF 2-BROMOBUTANE OVER SOLID CATALYSTS

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Stereochemistry of dehydrobromination of 2-bromobutane over KOH-silica has been determined from the composition and the deuterium content of each butene obtained from erythro-2-bromobutane-3-d_1. Below 250°C anti elimination was the preferred mode and syn elimination above 250°C.

Few have been reported concerning the stereochemistry of elimination reactions over solid surface, although the steric course of reaction is expected to be closely connected with the reaction mechanism and the geometry of active sites.[1,2] We observed previously that the dehydrobromination of meso- and dl-2,3-dibromobutanes took place selectively by anti elimination over some basic catalysts.[3] Recently, Kibby, Lande and Hall[4] demonstrated that syn elimination was favored over hydroxyapatite and anti elimination over alumina in the case of dehydration of 2-butanol. We studied the elimination reaction of 2-bromobutane and found that its stereoselectivity varied depending on reaction temperature and catalyst.

A pulse techique described elsewhere was utilized.[3] The deuterium content of each butene was determined by mass spectrometry after the products were separated gas chromatographically. 2-Bromobutane-d_0(I) was obtained commercially (Tokyo Kasei, GR). erythro-2-Bromobutane-3-d_1(II) was prepared from DBr and trans-2-butene under UV irradiation at -70°C.[5] The conformational purity was 90% as determined by the stereoselective dehydrobromination in alcoholic KOH solution.[5] KOH-silica was prepared by impregnation of silica gel (Wako Chemicals, Q-12) in KOH solution. Typical butene compositions from I and II (normalized to 1-butene) and d_1% from II (butenes contained only d_0 and d_1 species) are given in Table I. No isomerization of butenes occurred under these conditions. In the table, it is seen that deuterium substitution at 3 position decreased the formation of 2-butenes relative to 1-butene. The effect was larger for trans-2-butene than for cis-2-butene at 95°C($3.4/2.0 > 2.7/2.4$), but larger for cis-2-butene at 300°C($1.4/1.1 > 1.2/1.1$). Inversion of the effect took place at about 250°C. These results may be explained as the results of isotope effects. 1-Butene formation should little be affected by the deuterium atom at 3 position. However, 2-butene formation is expected to change depending on the stereochemistry; in anti elimination dehydrobromination of II gives cis-2-butene-d_1 (primary isotope effect) and dedeuterobromination of II gives trans-2-butene-d_0 (secondary isotope effect), so that the formation of trans-2-butene should be more retarded than that of cis-2-butene. In syn elimination, reverse effect is expected.

Table I: Dehydrobromination of 2-Bromobutane-d_0 and erythro-2-Bromobutane-3-d_1 over KOH-SiO_2

Temp. °C	Bromobutane	Butene composition and d_1% (in parentheses)[a)] 1-Butene	trans-2-Butene	cis-2-Butene	anti %[b)]	Primary isotope Effect[b)]
95	I (d_0)	1.0	3.4	2.7	87	1.9
	II (d_1)	1.0(98)	2.0(33)	2.4(86)		
300	I (d_0)	1.0	1.2	1.4	32	1.4
	II (d_1)	1.0(96)	1.1(71)	1.1(43)		

a)Corrected for butene-d_0's from 2-bromobutane-d_0 which was contained in II (3%).

b)Estimated assuming that the isotope effects for anti and syn eliminations to form trans- and cis-2-butenes are same.

Therefore, the results indicate that anti elimination was the preferred mode below 250°C and syn elimination above 250°C.

The change in stereoselectivity was confirmed by the deuterium content of the products given in the table: higher deutrium content in cis-2-butene than in trans-2-butene at 95°C and that in trans-2-butene at 300°C. Per cent of anti elimination and the isotope effects estimated according to Kibby et al.4) from the butene composition and the deuterium content are given in the table. The variation of stereoselectivity with the reaction temperature is tentatively explained as follows. Anti elimination was favored enthalpically (lower activation energy),6) but less favored entropically because a special arrangement of two active sites seems to be necessary for anti elimination,1) so that anti elimination prevailed at low temperature and syn elimination at high temperature.

It was indicated from the butene compositions that syn elimination was preferred over silica gel at 100-300°C and anti elimination over alumina below 200°C. Elimination of 2,3-dibromobutane proceeded by anti elimination over these catalysts. Thus, the stereochemistry of elimination reaction varies depending on the reactant, the reaction temperature and the catalyst.

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