JOURNAL OF CATALYSIS 33, 474–479 (1974)

Stereoselectivity of the Elimination Reactions of 2,3-Dihalobutanes and 2-Bromobutane Over Alkaline Earth Metal Oxides and Alumina

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Received December 13, 1973

The stereochemistry (*anti* or *syn* mode) of dehydrohalogenation of 2,3-dibromobutane, 2,3-dichlorobutane and 2-bromobutane over MgO, CaO, SrO and Al_2O_3 was determined by use of a pulse technique from the products of the diastereomeric isomers of each compound at 100–250°C. The elimination of hydrogen halide proceeded selectively by *anti* mode over *fresh* surface of these oxides below 200°C for dibromobutane and below 250°C for dichlorobutane, reflecting the surface basicity. *Anti* mode was also favored in the case of 2-bromobutane at about 100°C. However, due to the alteration of surface basicity by hydrogen halide formed, the stereoselectivity decreased with repeated pulses.

Present results agree with the idea deduced previously in the case of silica gels that the acid–base properties of catalyst and substrate are the prime factor controlling the steric course of reactions. Stereochemistry of debromination and halogen-substitution reactions of dibromobutane, the accompanying reactions, was also determined to be *anti* mode and retention, respectively.

INTRODUCTION

Stereochemical studies of reactions over catalyst surfaces are useful not only for the elucidation of reaction mechanism, but also for the characterization of active surface sites. In contrast to liquid-phase reactions, active sites are immobile and there is no solvation on the solid surface, so that different factors may play important roles in determining the steric course of reaction. Various factors such as steric effects, timing of bond rupture or formation and shape of reaction intermediate have been suggested (*1–3*).

We found previously that the steric course of dehydrohalogenation of alkyl bromides over alkali-treated silica gel varied remarkably depending on the catalyst and substrate (*4*). Dehydrobromination of 2-bromobutane, for example, proceeded by *anti* mode over KOH–SiO_2 but *syn* mode over SiO_2. These results were interpreted by the idea that the primarily important factor determining the steric course of reaction is the acid–base properties of substrate and catalyst. When the surface becomes more basic or the β-proton of the substrate becomes more acidic, the rupture of two bonds occurs more concertedly, leading to *anti* elimination. The primary aim of the present work was to determine the stereochemistry of dehydrohalogenation over alkaline earth metal oxides and alumina and to examine the applicability of the above hypothesis.

It has recently been reported that oxides of alkaline earth metals reveal strong basicity (*5a, 6*) and high catalytic activity for butene isomerization (*6, 7*) when evacuated at 400–500°C. The observed basicity was fairly well correlated with the catalytic activity for dehydrochlorination (*5b*). If the acid–base properties play decisive roles in determining the stereochemistry, *anti* elimination should be favored over these oxides, since CaO, MgO and SrO are more strongly basic than KOH–SiO_2. On the contrary, if the surface structure is more important, different stereochemistry may be expected, because their surface structures seem much different from silica gel (e.g., surface area of CaO was 6 m^2/g). Noller, Hantsche and Andreu (*8*) reported that dehydrochlorination of dichlorobutane over CaO was completely non-stereoselective. However, the surface basicity of these oxides is very sensitive to the method of activation (*6*) and, further, poisoned by H_2O, CO_2 (*6*) and O_2 (*7*). Moreover, in the elimination reaction of hydrogen halide, acidic hydrogen halide formed by the reaction would inevitably change the nature of basic sites. Thus, it seems worthwhile to reexamine the stereochemistry of the reactions over fresh basic sites of the oxides.

Experimental Methods

Apparatus and procedure. A conventional pulse technique described elsewhere was utilized (*4*). Catalysts (30–600 mg) were preheated in a reactor at 300–390°C for 1.5 hr in the stream of dry deoxygenated helium (40 ml/min). Since the activity of CaO for butene isomerization was revealed by pretreatment above about 370°C, alkaline earth metal oxides were ordinarily preheated at 350°C. This ordinary pretreatment was sufficient to develop strong surface basicity which turned 2,4-dinitroaniline ($pK_{BH} = 15.0$) to its basic color. It was necessary to keep the rate of temperature-rise and the flow rate of helium constant during the pretreatment in order to obtain reproducible results. After the catalyst was cooled to the reaction temperature, the flow rate of helium was increased to 60 ml/min and alkyl halide (1 or 2 μl for each pulse) was injected intermittently with aid of a microsyringe. Products were analyzed as described previously (*4*).

Catalyst. MgO, CaO and SrO were prepared by the calcination of basic magnesium carbonate at 600°C, of calcium carbonate at 950°C and of hydrated strontium hydroxide at 850°C. Their basicities have been reported previously (*5a*). Al_2O_3 was prepared by the calcination of hydrated alumina (Alcoa C-35) at 530°C for 7 hr. $CaCl_2 \cdot 6H_2O$ (Kanto Chemicals Ltd., GR grade) was used after heating at 110°C overnight and grinding to a powder.

Reagents. 2,3-Dibromobutanes (C_4Br_2) and 2,3-dichlorobutanes (C_4Cl_2) were prepared by the methods described previously (*4*). Their diastereomeric purity was 97 and 99% for *meso-* and *dl*-C_4Br_2, and 98 and 93% for *meso-* and *dl*-C_4Cl_2, respectively. 2-Bromo- and 2-chlorobutane (C_4Br and C_4Cl) were of GR grade obtained commercially from Tokyo Kasei Ltd. *erythro*-2-Bromobutane-3-d_1 prepared as described before (*4*) contained 7% of d_0 species and 16% of *threo* form. *cis*-2-Bromo-2-butene was prepared by *anti* elimination of *meso*-C_4Br_2 in an alcoholic KOH solution and purified by gas chromatographic separation.

Results

Reaction of 2,3-dibromobutane. In Figs. 1 and 2, products from the first pulse of *meso*-C_4Br_2 over MgO and CaO are shown as a function of reaction temperature. As described below, results carefully obtained from the first pulse reflect the nature of the fresh catalyst surface. In the experiments presented in Figs. 1 and 2, HBr elimination was kept at 30–50% conversion by changing the amount of catalyst. Reactions

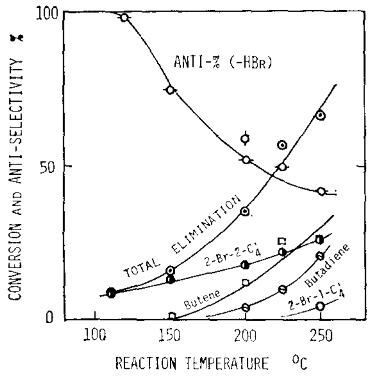


FIG. 1. Products from the reaction of *meso*-2,3-dibromobutane over MgO. Conversions are normalized to those over 30 mg of MgO. (⊙) Total elimination reaction; (-○-) *anti*%, *cis*/(*trans* + *cis*) ratio of 2-bromo-2-butene from *meso* form; (ϕ) *anti*%, *trans*/(*trans* + *cis*) ratio of 2-bromo-2-butene from *dl* form.

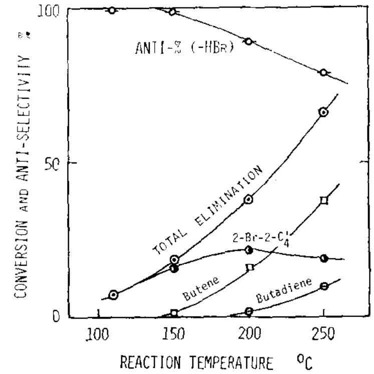


FIG. 2. Products from the reaction of *meso*-2,3-dibromobutane over CaO. Conversions are normalized to those over 50 mg of CaO. Symbols are the same as in Fig. 1.

observed were 2,3-HBr elimination to form 2-bromo-2-butenes, butadiene formation and debromination leading to 2-butenes. The latter two reactions rapidly increased with the reaction temperature. In addition, considerable isomerization to *dl*-form occurred. Above 250°C over MgO small amounts of 2-bromo-1-butene and an unidentified products (which appeared closely after *cis*-2-bromo-2-butene in a gas chromatogram) also formed.

Stereoselectivity of elimination reactions was estimated by the *trans* to *cis* ratio of 2-bromo-2-butene and 2-butene in the products, since *meso*-C_4Br_2, for example,

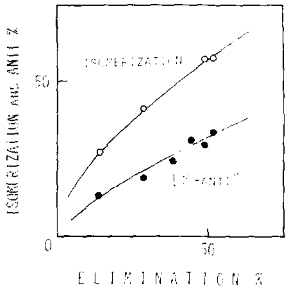


FIG. 3. *Anti%* and extent of isomerization vs elimination in the reaction from the first pulse of *meso*-2,3-dibromobutane over MgO at 150°C. Isomerization = 100 × *dl*/(*meso* + *dl*) of C_4Br_2; 100-*anti%* = 100 × *trans*/(*trans* + *cis*) of 2-bromo-2-butene.

gives *cis*-2-bromo-2-butene and *trans*-2-butene by *anti* elimination. Isomerization of 2-bromo-2-butene and 2-butene did not occur under the present reaction conditions. As the *anti*-selectivity (*anti%*) of 2,3-HBr elimination given in Figs. 1 and 2 shows, the reaction proceeded very stereoselectively by *anti* elimination at about 100°C over both oxides, but the selectivity decreased at higher temperatures. Stereoselectivity of debromination approximately paralleled that of HBr elimination. Reaction of dibromobutane over SrO and Al_2O_3 also took place by *anti* mode as shown in Table 1.

In Fig. 3, 100-*anti%* and the extent of

TABLE 1

REACTION PRODUCTS FROM ELIMINATION REACTIONS OF 2,3-DIHALOBUTANES OVER VARIOUS SOLIDS

						Products (%)				
								2-Bromo-2-butene		
Catalyst	Wt (mg)	Pretreatment temp (°C)	Reaction temp (°C)	Reactant	No. of pulse	Butene	Butadiene	*trans*	*cis*	*Anti* %[a]
SrO	308	350	150	*meso*-C_4Br_2	1st	0	0	0.3	7.0	99
Al_2O_3	154	300	152	*meso*-C_4Br_2	1st	3	11	8	41	86
MgO	53	350	250	*meso*-C_4Cl_2	1st	0	2.0	6.2	39.0	87
MgO	49	350	250	*dl*-C_4Cl_2	1st	2.6		43.1	8.2	89
CaO	76	350	250	*meso*-C_4Cl_2	1st	1.5		4.1	26.4	88
					2nd	0.9		2.6	6.8	73
					3rd	0.9		2.4	4.2	64

[a] *Anti*-selectivity of 2,3-HBr elimination, viz, *cis*/(*trans* + *cis*) from *meso* form or *trans*/(*trans* + *cis*) from *dl* form, corrected for the diastereomeric purity of the reactant.

TABLE 2
REACTION PRODUCTS FROM 2,3-DIBROMOBUTANE OVER MgO AND $CaCl_2$ AT 150°C

No. of pulse	Reactant	Products (%)								
		2-Butene		Butadiene	2-Bromo-2-butene		2-Chloro-3-bromobutane		2,3-Dibromobutane	
		trans	*cis*		*trans*	*cis*	*erythro*	*threo*	*meso*	*dl*
					MgO (55 mg)					
1	*meso*	4.5	2.0	0.5	5.5	23.0	—	—	40.0	24.5
2	*meso*	3.9	2.3	0.6	2.1	4.5	—	—	47.0	40.0
3	*meso*		4.0		2.0	1.5	—	—	50.0	41.5
21[a]	*meso*	0.9	0.1	3.3	1.0	0.4	5.4	0.9	83	5[b]
23[a]	*dl*	0.1	0.8	3.1	1.2	0.3	Tr	4.5	1	89
					$CaCl_2$ (278 mg)					
1[c]	*meso*	2.7			1.6	0.5	40.5	6.4	39.4	5.5[b]
2[d]	*dl*	3.2			3.7		2.6	41.3	3.8	41.9

[a] Prior to each of these pulses, 2 μl of 2-chlorobutane was pulsed.

[b] Not accurate.

[c] 2.7% of 2,3-dichlorobutane (mainly *meso* form) was observed in the products together with 0.7% of 2-chloro-2-butene.

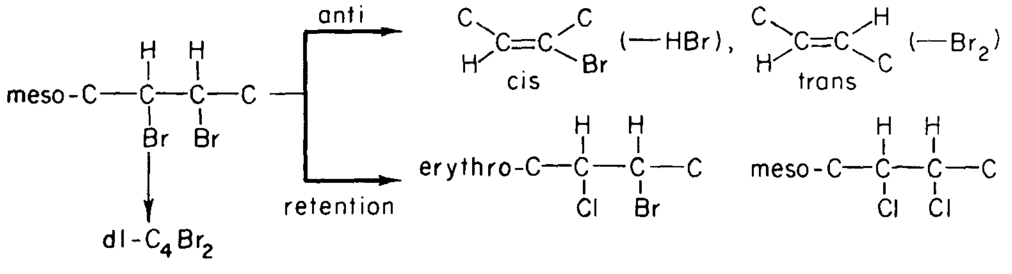
[d] 3.5% of 2,3-dichlorobutane was formed.

isomerization of C_4Br_2 obtained from the first pulses are plotted against the elimination in the case of *meso*-C_4Br_2 over MgO at 150°C. Figure 3 shows that the isomerization considerably lowered the apparent selectivity. In fact, the *anti*-selectivity extrapolated to zero conversion was almost 100% in this case.

Variation of products upon repeated pulses. At the initial stage, products varied rapidly from pulse to pulse, as typical results given in Table 2 show. Over fresh catalyst (first pulse), main reaction was 2,3-HBr elimination by *anti* mode, accompanied by a minor reaction of debromination which was also *anti* elimination. As the number of pulses increased, 2,3-HBr elimination, together with its stereoselectivity, diminished rapidly. After several pulses, HBr elimination products from *meso*- and *dl*-C_4Br_2 became almost identical. It is to be noted that debromination proceeded mainly by *anti* mode after the isomerization of C_4Br_2 disappeared finally.

Substitution reactions. Substitution (exchange) of halogen was observed in the reaction of C_4Br_2 pulses, subsequent to the injection of C_4Cl or C_4Cl_2 pulses, or in the reaction of the latter after C_4Br or C_4Br_2 pulses (Table 2). These results indicate that part of hydrogen halide formed stayed on the surface. It is noteworthy that *erythro*-2-chloro-3-bromobutane was formed from *meso*-C_4Br_2 and *threo*-form from *dl*-C_4Br_2, i.e., the stereochemistry of the substitution reaction was *retention*. *erythro*- and *threo*-2-chloro-3-bromobutane were identified by comparing the gas chromatographic retention times of two peaks (*erythro* and *threo*, 12.8 and 14.1 min) as well as those of *meso*- and *dl*-C_4Cl_2 (5.8 and 6.7 min) and C_4Br_2 (22.3 and 24.5 min) with those in the literature (*9*). The identification was confirmed by the existence of the same two peaks in the gas chromatographic analysis of the products from *meso*- and *dl*-C_4Cl_2. This stereoselective substitution reaction between substrate and solid predominated in the reaction of C_4Br_2 over $CaCl_2$ (Table 2).

The reactions of C_4Br_2 are summarized for *meso*-form by the following scheme.



Reaction of 2,3-dichlorobutane. Results with MgO and CaO are given in Table 1. High *anti*-selectivity is seen from the *cis/trans* ratio of 2-chloro-2-butene over both oxides. This result is not in agreement with those reported by Noller, Hantsche and Andreu (*8*). Decreases in the stereoselectivity from pulse to pulse were also observed.

Dehydrobromination of 2-bromobutane. Butene composition in the products from 2-bromobutane changed rapidly with the repeated pulses. Further, the catalytic activity of the changed surface was high at the reaction temperatures higher than about 160°C. Therefore, the stereoselectivity was determined on the first pulse at reaction temperatures as low as 90–110°C. At these temperatures, the catalytic activity of the changed surface is low, so that the influence on the results by the reaction which might take place over the changed surface can be minimized. No isomerization took place even during the elimination reaction, as evidenced by the absence of isomerization of 1-pentene, which was injected together with 2-bromobutane and was found to be more reactive than butenes over fresh CaO preheated at 390°C.

Results are presented in Table 3. The higher content of d_1 species ($d_1\%$) of *cis*-2-butene relative to *trans*-2-butene demonstrates that *anti* elimination is the favored mode over these catalysts. *Anti*-selectivity given in Table 3 was roughly estimated from the $d_1\%$ by use of the previous equations (*2*, *4*) on the assumption that the *anti*% and isotope effects are identical for *trans*- and *cis*-2-butene formations. Calculated isotope effects were about three. After several pulses, the reaction became nearly non-stereoselective.

DISCUSSION

Stereochemistry of HBr elimination. Present results demonstrated that *anti* elimination is the preferred mode on fresh surface of MgO, CaO, SrO and Al_2O_3. If the isomerization of the reactant is taken into account, the reactions were very stereoselective below 200°C for C_4Br_2 and below 250°C for C_4Cl_2. The apparent *anti*-selectivity was in the order of SrO $\gg$ CaO $>$ MgO $\sim$ Al_2O_3 which is consistent with

TABLE 3

DEHYDROBROMINATION OF *erythro*-2-BROMOBUTANE-3-d_1 OVER VARIOUS OXIDES

Catalysts	Pretreatment temp (°C)	Reaction temp (°C)	Butene composition[a] ($d_1\%$ in parentheses) 1-	*trans*	*cis*	*Anti*%[b]
CaO	350	110	1.0 (94)	0.42 (50)	0.51 (83)	84
MgO	390	100	1.0 (90)	0.6 (57)	0.8 (81)	76
Al_2O_3	300	110	1.0 (94)	2.0 (47)	3.9 (76)	79

[a] Butene compositions from 2-bromobutane-d_0 normalized to 1-butene and the content of d_1 species in each butene isomer from *erythro*-2-bromobutane-3-d_1 are given.

[b] Percentage of reaction which proceeded via *anti* mode. See text.

the base strength measured (*5*). The order among alkyl halides, $C_4Cl_2 > C_4Br_2 > C_4Br$, was the same as in the previous work (*4*) and seems to reflect the acidity of β-protons. Thus, these results agree with the previous postulate mentioned in the Introduction. Present results contradict those reported by Noller, Hantsche and Andreu (*8*) who observed complete non-stereoselectivity over CaO. This may be due to the fact that their CaO was not pretreated sufficiently to reveal strong basicity or that their results might have been obtained on surfaces which were already changed by the reaction with hydrogen chloride.

Reaction mechanisms. The isotope effect found for C_4Br-3-d_1 and the *anti*-selectivity indicate that dehydrohalogenation proceeded by a concerted mechanism over fresh surface. The higher reactivity of dihalobutanes relative to 2-halobutanes is in accord with this mechanism, since β-halogen accelerates a concerted elimination reaction. After the rapid change of catalyst surface occurred, due to the reaction with hydrogen halide, the reaction possibly proceeds by the carbonium-ion mechanism suggested by Noller, Hantsche and Andreu (*8*). Non-stereoselectivity, the existence of halogen exchange and the higher reactivity of 2-halobutane than dihalobutane at the later stages support the idea that the carbon–halogen bond breaks first. Indicator test by benzeneazodiphenylamine ($pK_A = 1.5$) revealed that the surface of alkaline earth metal oxides became acidic after several pulses of reactants.

Anti-selectivity of debromination and the retention of configuration in halogen exchange may be explained by a concerted mechanism or by the interaction of a β-bromine with a C^+-center in a carbonium-ion intermediate which prevents the rotation about the C–C bond. Substitution reactions in the liquid phase by S_N1 mechanism retain original configuration when Br or COO^- exists at the β-position (*10*). Butadiene was most likely formed by the hydrogen halide elimination from 3-halo-1-butene which is the product of 1,2-dehydrohalogenation of 2,3-dihalobutane. 3-Chloro-1-butene produced butadiene very readily under the present reaction conditions.

ACKNOWLEDGMENTS

The authors are grateful to Professor Y. Saito and Dr. J. Take for useful discussions and to Messrs. S. Asao, N. Tani and Y. Aoki for assistance in the preparation of reagents and mass spectrometric analyses. Financial support in part by the grant from the Ministry of Education is acknowledged.

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