JOURNAL OF CATALYSIS 29, 385–394 (1973)

Elimination Reactions of 1-Chlorobutane and 2-Chlorobutane Over X and A Zeolites Containing Different Cations

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Received July 24, 1972

The reactions were studied in the temperature range from 150–400°C using a flow reactor. Linde 13X zeolite was converted to the Ca, Mg, Co, Ni, Cu, Pr forms, Linde 4A to the Zn form by replacing the sodium ions. With Ni and Cu, exchange of more than 80% led to a breakdown of the zeolite lattice. In addition to HCl, cracking and other products, the 4 butene isomers were produced over X zeolites with polyvalent cations (pore diam about 9 Å). No isobutene could be detected over 4A zeolites (pore diam approx 4 Å). By varying the contact time the three linear butenes could be shown to be primary products, whereas isobutene was formed in a consecutive step, mainly from *trans*-2-butene. A nearly linear relationship was obtained between the strength of the electrostatic field of the cations inside the zeolite cages (X zeolites) and isobutene formation. With the exception of the NaX the activation energies showed no remarkable differences (from 12 to 15 kcal/mol with 2-chlorobutane), but correlated with the electrostatic field strength of the cations. Eliminations and isomerizations were found to proceed according to a carbonium ion (E1) mechanism, with the exception of NaX (below 200°C), NaA and ZnA.

INTRODUCTION

In recent years synthetic faujasites have become important commercial catalysts. The importance of these substances, normally called molecular sieves, may be seen from the large number of papers dealing with their synthesis (*1*), structure (*1, 2*) and catalytic properties (*3, 4*). Most of the former studies are concerned with isomerization, alkylation, cracking, hydrocracking, polymerization, etc. However, little is known about dehydrohalogenation (*5, 6*).

In previous papers about elimination reactions, Noller, Andréu, and Hunger (*7*) have pointed out that the activity of salt catalysts is clearly related to the size and charge of the cations as well as to the basicity of the anions, the influence of the cations being more pronounced. The activity of the cations should increase with their electron pair acceptor strength, which is certainly dependent upon their electrostatic field.

For studying the influence of the cations, it would be convenient to have a series of catalysts with only the cation varied. This is difficult to realize with salt catalysts, since also the crystal structure may be affected. With molecular sieves, however, the cation can be varied without affecting notably the "anion." In this study Linde 13X and 4A molecular sieves were used with alkali earth, transition metal and rare earth cations.

EXPERIMENTAL METHODS

Apparatus

Most experiments were carried out with a flow reactor made of Vycor glass tube, 8 mm in diameter, with 0.1 to 0.5 g of catalyst supported on glass wool. A stream of dry nitrogen (40 ml/min, p.a. quality) passed through a thermostated saturator containing the reactant. The reactions were run under atmospheric pressure of the gas mixture. Rough values of reaction times could be estimated from the void space in the catalyst zone and the flow rate of the reaction mixture (carrier gas + reactant). The amount of reactant in the feed was determined by condensation of the reactant. Catalyst calcination was effected immediately prior to reaction in a separate vacuum system, at 300°C and 10^{-2} Torr for 6 hr, with subsequent transfer to the reactor. Samples for gas chromatographic analysis were taken by Hamilton syringes after absorbing HCl with soda lime.

The microcatalytic technique (*8*) was used for studying the isomerization of *n*-butenes over NaX and ZnX in the absence of HCl.

A Perkin-Elmer Mark II Model F 11 with FID was used. The four butene isomers were separated by the following technique: column: 8 m; ⅛ in.; 20% propylene carbonate on Chromosorb P-AW 60/80 mesh; temp: 0°C; carrier gas: nitrogen, 30 ml/min; retention times: 1-butene, 6 min 18 s; isobutene, 6 min 49 s; *trans*-2-butene, 7 min 37 s; *cis*-2-butene, 8 min 55 s.

Catalysts

The catalysts were prepared from Linde 13X and Linde 4A molecular sieves.

A 60/80 mesh NaX zeolite from Union Carbide was used. Cation exchange was carried out with 250 ml 10% solutions of the appropriate salts (sulfates, chlorides, acetates) and 5 g zeolite at 90°C or below (see Table 1). The pH of the solution was held above 5 in order not to destroy the crystal lattice. ZnA was prepared in a similar way. The Pr-exchanged zeolite was prepared in a 5% solution of $Pr_2(SO_4)_3$, buffered with CH_3COOH/CH_3COONa in order to avoid the lowering of the pH caused by the acidic hydrolysis of the sulfate. Hereby only 42% of the sodium was exchanged.

The degrees of exchange were determined by complexometric titration with ethylenediaminetetraacetic acid (EDTA) of the salt solution before and after exchange and also by flame photometric and gravimetric analysis of the sodium in the exchanged zeolites (see Table 1).

X-Ray analysis of the catalysts showed no marked difference if they were prepared at a pH not lower than 5. Surface areas, as determined with nitrogen by the BET method, were between 480 and 500 m^2/g for all X zeolites, whereas A zeolites showed about 20 m^2/g (nitrogen did not enter into the pores).

Reactants

1-Chlorobutane, puriss. (G.C.) and 2-chlorobutane, puriss. (G.C.) were com-

TABLE 1

ZEOLITE PREPARATION

Zeolite	% Na exchanged		Salt	Exchange conditions		
	EDTA	Spectral and gravimetric[a]		pH	*T* (°C)	Time (hr)
CaX	68.3	—	$CaCl_2$	5.2	90	7
MgX	59.5	60.8	Mg-ac.	7.5	95	7
CoX	—	78.7	$CoCl_2$	5.0	95	7
NiX-1	51.0	—	$NiSO_4$	5.0	60	7
NiX-2	87.8	87.0	$NiSO_4$	5.0	90	8
CuX	39.8	—	Cu-ac.	5.5	20	5
ZnX	68.8	75.2	$ZnSO_4$	5.0	90	10
PrX	—	41.8	$Pr_2(SO_4)_3$	5.0	20	50
ZnA	82.0	—	$ZnSO_4$	5.0	95	9

[a] The values are the average of both methods.

mercial products (Fluka, Buchs, Switzerland) and were not purified further.

1-Butene, *trans*-2-butene and *cis*-2-butene were highly purified products for chromatographic use from Baker-Chemicals (Gross-Gerau, Western Germany).

RESULTS AND DISCUSSION

Conversion and Activation Energy

The kinetics were found to be first order with respect to the reactant, in agreement with earlier results (*7*).

$$k = \frac{1}{t} \ln \frac{c_0}{c_0 - x},$$

t reaction time, c_0 initial amount of reactant, x amount of butenes formed (equal to amount of HCl formed).

Since the flow rate of the (cold) carrier gas is maintained constant the reaction time is inversely proportional to the absolute temperature. The rate constant k is therefore given by

$$k = \alpha \cdot T \cdot \ln \frac{c_0}{c_0 - x} = A \cdot e^{-\Delta E_A/RT},$$

where α is a proportionality factor. Hence

$$\log\left(T \cdot \ln \frac{c_0}{c_0 - x}\right) + \text{const} = -\frac{\Delta E_A}{2.3 \cdot RT} + \log A.$$

The activation energy ΔE_A is calculated from the plot of log $\{T \cdot \ln[c_0/(c_0 - x)]\}$ against $1/T$.

Between 150 and 250°C the following order of activity (conversion) was obtained for X zeolites:

$Pr^{3+} > Mg^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Ca^{2+} > Cu^{2+} > Na^{+}$.

Conversions (at 200°C) and activation energies for all catalysts are compiled in Table 2.

2-Chlorobutane was found to be more reactive than 1-chlorobutane in agreement with earlier results (*7*). The activation energies and also the activities (conversions) obtained with different cation forms of X zeolites were rather similar, the greatest difference (6 kcal/mol) being that between NaX and PrX. With NaA, a markedly higher activation energy and lower activity was observed. In former studies with alkali and alkaline earth sulfates, differences of 10 kcal/mol and more have been observed (*9*). Obviously, the influence of the cations is less pronounced with zeolites than with salt catalysts.

The following interpretation of activation energies and activities may be given. As pointed out by Noller, Andréu and Hunger (*7*), a two-point interaction between reactant and catalyst must be assumed, this interaction always taking place between an electron pair acceptor

TABLE 2

COMPARISON OF CONVERSIONS AND ACTIVATION ENERGIES

Reactant	Catalysts	Conversions (%) at 200°C	ΔE_A (kcal/mol)	Temp range (°C)
1-Chlorobutane	NaX	32.5	11.4	150–265
	ZnX	32.5	13.5	150–260
2-Chlorobutane	NaX	50	9.0	150–238
	CaX	53	11.9	155–250
	MgX	65	14.0	150–250
	CoX	60	12.5	145–200
	NiX-1	58	12.0	155–205
	CuX	41	13.0	150–240
	ZnX	62	13.9	148–235
	PrX	85	15.0	148–220
	NaA	6	17.8	245–300

and an electron pair donor site. At one point the catalyst is the electron pair acceptor and the reactant the electron pair donor, at the other point it is just the inverse. Electron pair acceptor and donor properties of the catalyst should be attributed to its cations and anions, respectively. In the reactant, the leaving groups Cl^- and H^+ operate as electron pair donor or electron pair acceptor, respectively.

With X zeolites, the "anion" is the same in all cases. So differences of activities and activation energies should be mainly due to differences of electron pair acceptor strength of the cations. This property should depend, at least to a high extent, upon their electrostatic field.

The electrostatic fields of cations in S_{II} sites, which are most important for catalysis, were calculated by Ward (*12*) with values from Rabo *et al.* (*23*).

A plot of our activation energies against their values is given in Fig. 1. A linear relationship is obtained.

With X zeolites the higher activity coincides with the higher activation energy (Table 2). This phenomenon was also observed in former studies of elimination reactions over salt catalysts. It has certainly to do with the so-called compensation effect (*7, 9, 10*), according to which the higher activation energy is in most cases combined with the higher frequency factor. If the temperature studied is above the temperature at which the Arrhenius lines intersect, activity (as given by the percentage of conversion) increases with activation energy.

Thus the higher activity is clearly related to the greater electric field of the cation. This relation between activity and electric field has also been found for dehydration (*24, 25*) and even for cracking reactions (*11*). It is especially obvious for alkali and alkaline earth cations. The high activity of Pr^{3+} could also be explained in this way. It may be noticed that cations with vacant *d* orbitals also fit this relationship (Fig. 1). So vacant *d* orbitals, which normally are considered to be of high importance in catalysis, may be supposed to be less important for dehydrohalogenation. No relationship between *d*-vacancies and activity can be seen from Table 2. On the other hand, the surprisingly high activity of Zn^{2+}, which has often been reported in recent years (*7, 12–16*), makes one think of its *d*-configuration, which is clearly different from that of Mg^{2+}. Although the two ions have different radii, their activity is roughly equal.

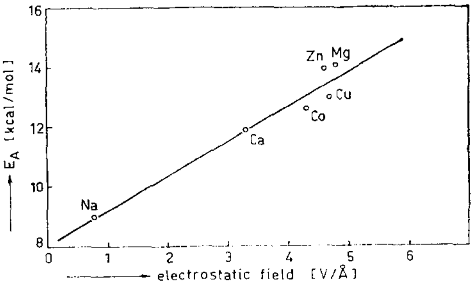


FIG. 1. Activation energy and electrostatic field (*12*).

The above discussion does not take into account the electron pair donor sites of the catalyst. In former studies (*7*) a rough correlation between the basicity of the anions and the catalytic activity has been observed. In zeolites the sites with higher electron pair donor strength should be the $[AlO_4]^-$ tetrahedra, the basicity of which is probably higher than that of $[SO_4]^{2-}$, for example, which has been studied earlier. The high activity of zeolites compared to salt catalysts is due to this difference in electron pair donor strength of the anionic sites. For the same reason the differences of the cations, so pronounced with salt catalysts, are smaller with zeolites.

Product distribution

2-Chlorobutane over X zeolites. The distribution of the butenes from 2-chlorobutane over MgX is shown in Fig. 2. All experiments were run under the same conditions, with 0.1 g of catalyst in the reactor and a reaction time of roughly 0.2 s.

With all X zeolites, the percentage of the three linear butenes relative to one another was close to equilibrium in the whole temperature range. With very active X zeolites like MgX and ZnX, the thermodynamic equilibrium of all four butenes

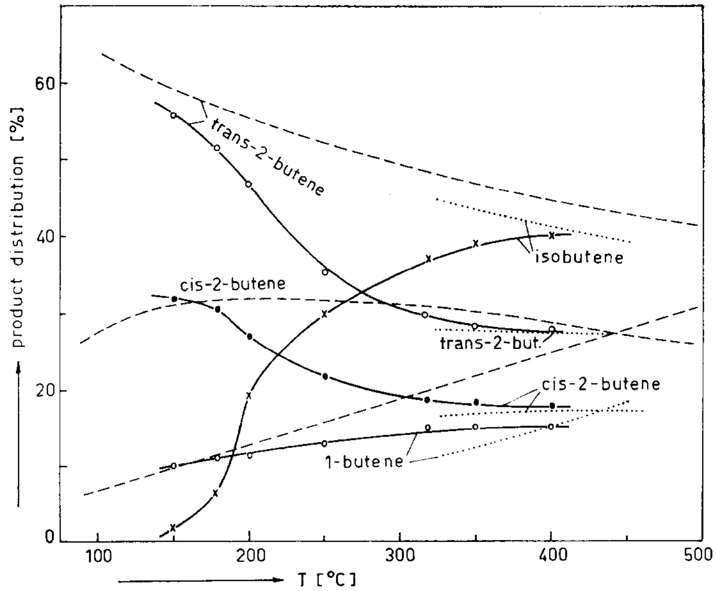


Fig. 2. Reaction of 2-chlorobutane over Mg X. (0) 1-Butene; (×) isobutene; (○) *trans*-2-butene; (●) *cis*-2-butene; (— —) thermodynamic equilibrium of the *n*-butenes; (· · · ·) thermodynamic equilibrium of all 4 butenes; residence time about 0.2 s.

was reached at temperatures near 400°C. No other products than *n*-butenes and HCl were detected below 140°C with any X zeolite. Beyond 140°C, isobutene and also cracking and other products, like propene, propane, butane, ethylene, ethane, butadiene were formed, their amount increasing with temperature. With the most active catalysts, i.e., Pr-, Zn- and MgX, these by-products were formed to an extent of 60–70% of the total yield at 400°C. The distribution of the butene isomers is given in Table 3 for all X zeolites.

In Table 3, ZnX appears to be the most active catalyst for isobutene formation. However, PrX was only 42% exchanged. To compare PrX with ZnX, a ZnX sample was prepared with roughly the same degree of exchange. Thus the order of isobutene formation in the temperature range 150–350°C was found to be:

$$Pr^{3+} > Zn^{2+} > Mg^{2+} > Co^{2+} > Ni^{2+} > Ca^{2+} > Cu^{2+} > Na^{+}.$$

The activity pattern for isomerization is similar to that for elimination. The only inversion is Zn^{2+} and Mg^{2+}. It is likely that isomerization activity is governed by the

TABLE 3

Percentage (Sum of Butenes = 100%) of All Butenes Formed Over X Zeolites at 250°C (Residence Time About 0.2 s)

Zeolite	1-Butene	Isobutene	*trans*-2-Butene	*cis*-2-Butene
CaX	16	9.5	46.5	28
MgX	13	30	35	22
CoX	15	9.5	46.5	29
NiX-1	16	9.5	46	28.5
NiX-2[a]	16	12	44	28
CuX[b]	16	6	49	29
ZnX	9	35	35	21
PrX	12	29	48	21

[a] 87.8 exchanged NiX was destroyed in the temperature range from 350 to 400°C, as indicated by a rapid drop in isobutene formation. 92% exchanged NiX had a destroyed crystal lattice (X-ray analysis) before reaction was started. No isobutene was formed with it. NiX destruction also has been mentioned by Nishizawa *et al.* (*14*). A similar effect could not be detected with CoX.

[b] The crystal structure of CuX breaks down at degrees of exchange from 70 to 100%, as detected by X-ray analysis. Then no isobutene is formed. Dimitrov and Leach (*17*) gave a detailed description of CuX zeolites and their behavior at different degrees of exchange.

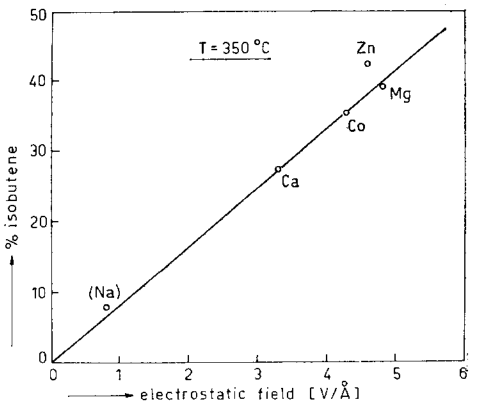


FIG. 3. Isobutene formation and electrostatic field (*12*) at a reaction temperature of 350°C.

same factors as elimination activity. A straight line is obtained, when the activity is plotted against the electric field (Fig. 3), as given by Ward (*12*). The low activity of CuX was also observed by Ward (*12*) for *o*-xylene isomerization.

With reduction of the reaction time the relative isobutene yield became smaller and the *n*-butenes were obtained in thermodynamic equilibrium (Fig. 4). Obviously the equilibrium of the *n*-butenes was established immediately, whereas isobutene formation occurred in a subsequent adsorption step.

Figure 5 shows isobutene formation as a function of time of reaction. The shape of the curves for Mg- and ZnX is due to several factors (coke formation, HCl), which are difficult to discuss. There was an obvious difference between Mg- and ZnX on the one hand and NaX on the other. NaX did not display activity for skeletal isomerization in the first minutes of reaction. However, as the reaction goes on, HCl is produced and Na^+ is partially replaced by H^+, the isomerization activity of which is observed after about 15 min.

$$NaX + HCl_{ads} \rightarrow HX + NaCl_{ads}.$$

If this is true NaCl should be analytically detectable. After a run of 3 hrs at 300°C, 2 g of NaX were extracted in bidistilled water. Na (82.7 mg) (35% of the total Na content in the zeolite) was found in the liquid phase, produced by this reaction. This corresponds to about 10% of HCl produced within 3 hr. In Fig. 5, isobutene formation begins after about 15 min, when only a small amount of Na^+ has been exchanged. So a considerable activity of the exchanged centers must be assumed. A similar result was described by Matsumoto, Yasui, and Morita (*18*) and interpreted as an induction effect.

Isomerization of n-butenes over NaX and ZnX (microcatalytic technique)

From the above experiments the question arises whether or not HCl is necessary for

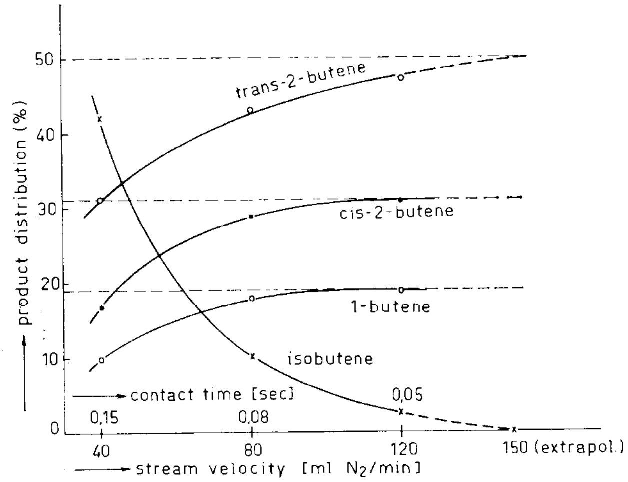


FIG. 4. Product distribution at different residence times with the same symbols used as in Fig. 2. Catalyst, ZnX; reactant, 1-chlorobutane; *T*, 300°C; (— —) thermodynamic equilibrium of the *n*-butenes.

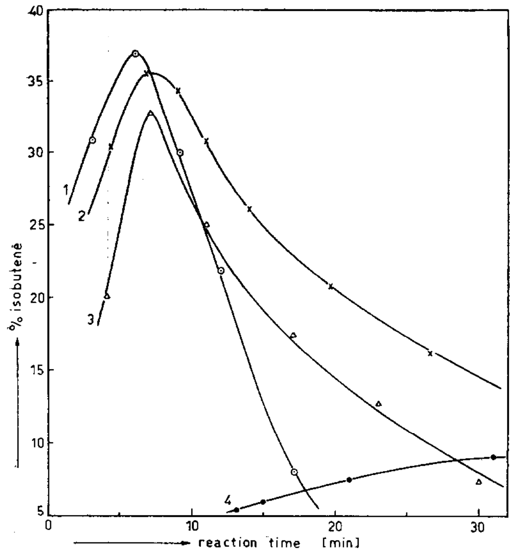


FIG. 5. Isobutene formation as a function of reaction time; reactant: 2-chlorobutane; catalysts: (1) ZnX (*T*, 250°C); (2) MgX (*T*, 300°C); (3) MgX (*T*, 250°C); (4) NaX (*T*, 300°C).

TABLE 5
PERCENTAGE OF THE *n*-BUTENES FORMED OVER 4A ZEOLITES AT 250°C (CONTACT TIME ABOUT 0.2 s)

Zeolite 4A	Degree ex. %	Bu-1	Iso	*trans*	*cis*
Na-4A	—	16.5	—	35	48.5
Zn-A	82	13.5	—	41	45.5

isobutene production at all. To answer it, microcatalytic studies (*8*) of the isomerization of the *n*-butenes were made. Furthermore, it was interesting to see if the disposition of the three linear butenes toward isobutene formation was equal. Table 4 gives the results. No isobutene was obtained over NaX, whereas *n*-butenes were easily formed. ZnX on the other hand gave isobutene, with *trans*-2-butene being more reactive for this isomerization than both 1-butene and *cis*-2-butene.

2-Chlorobutane over 4-A zeolites. Product distributions with NaA and ZnA were markedly different from those with X zeolites (Fig. 6). No isobutene or cracking products could be detected. 4A zeolite has a pore diameter of about 4 Å only, whereas the diameter of the reactant is roughly 6 Å. Thus reaction takes place only on the "outer" surface, but not inside the pores. This suggests that isobutene formation is only possible inside the pores, where the electric field probably is stronger.

The butene distribution showed predominance of 2-butene, as observed usually, but with preference of *cis*-2-butene over *trans*-2-butene in the temperature range 150–400 and 150–250°C for NaA and ZnA, respectively. The percentage of *n*-butenes formed over 4A zeolites is shown in Table 5. ZnA produced somewhat more *trans*-2-butene. It is an almost general finding that the more active catalyst gives a product distribution closer to equilibrium; in other words, higher activity is normally accompanied by lower selectivity. The distribution of products is similar to that found by Noller, Löw and Andréu (*19*) over salts and oxides.

1-Chlorobutane over NaX and ZnX. ZnX gave nearly the same product distribution with 1-chlorobutane in the tem-

TABLE 4
DISTRIBUTION OF THE BUTENES OBTAINED OVER NaX AND ZnX BY PULSING *n*-BUTENES AT 300°C[a]

Butene pulsed	Zeolite	1-Butene	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cracking (%)
Butene-1	Na-13X	*47*	—	40	13	80
trans-2-		17	—	*57*	26	5–10
cis-2-		30	—	29	*41*	
Butene-1	Zn-X	*47*	18	28	7	80
trans-2-		14.5	47	*23.5*	15	15
cis-2-		59	18	19	*4*	19

[a] Pulsed butene italicized. Nitrogen flow velocity, 40 ml/min.

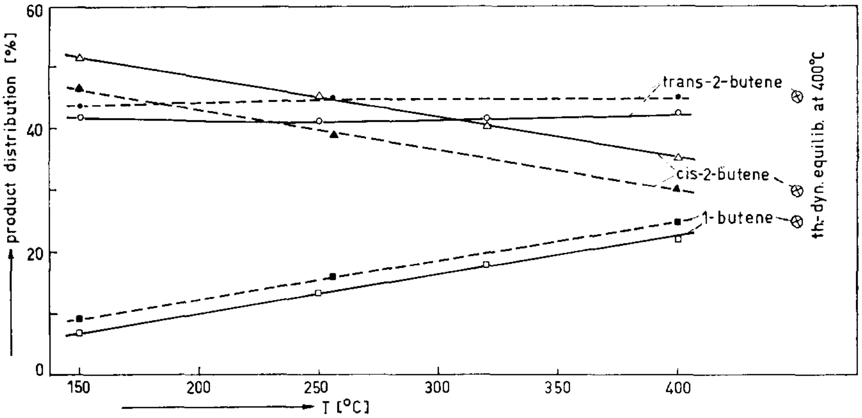


FIG. 6. Reaction of 2-chlorobutane over ZnA at different residence times. (——) 0.2 s residence time; (— —) 1.0 s residence time.

perature range between 150 and 400°C as with 2-chlorobutane. This is indicative of an E1 mechanism. In contrast to this, NaX showed a 1-butene predominance over 2-butenes till 200°C, as shown in Fig. 7, which shows the product distributions for each temperature after 15 min of reaction. Above 200°C, thermodynamic equilibrium of the *n*-butenes was nearly reached, with 1-butene always being somewhat above its equilibrium value. Isobutene formation was remarkably low, even at 400°C. However, when the reaction was run over a period of more than 15 min, isobutene formation considerably increased. NaX is the only X catalyst with a considerable E2 character (7) in the lower temperature range.

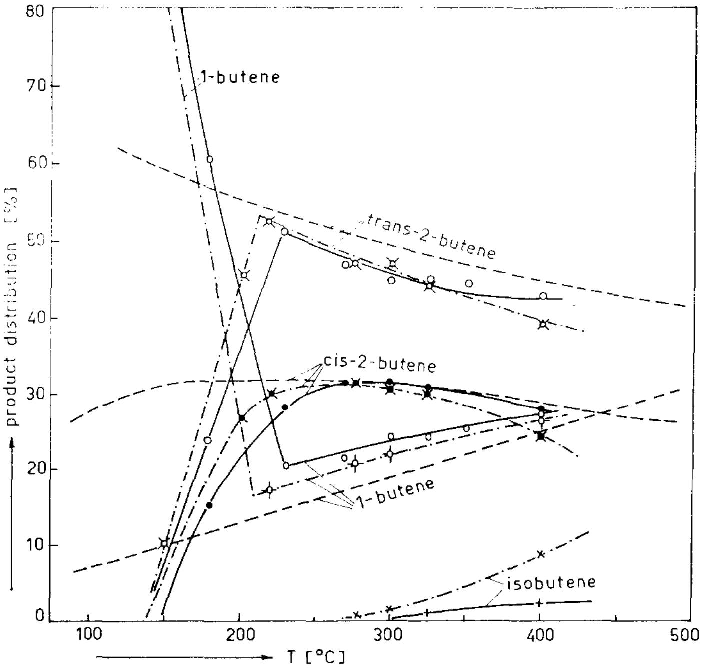


FIG. 7. Reaction of 1-chlorobutane over NaX symbols used are the same as in Fig. 2. (——) 0.2 s residence time; (-· -) 1.0 s residence time; (— —) thermodynamic equilibrium of the *n*-butenes.

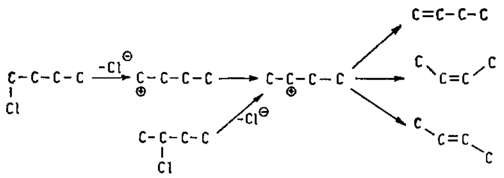
1-Chlorobutane over 4A zeolites. The product distribution with 4A zeolites showed a 1-butene predominance over the whole temperature range up to 400°C. The conversion was only a few percent (about 10% at 400°C). Consequently the elimination mechanism of 4A zeolites is E2, as found over some salts and oxides (*7*). No isobutene or cracking products could be detected.

Mechanism

In previous papers (*7, 26*), it has been pointed out that there are two preferred mechanisms, which are termed E1 and E2, like the corresponding mechanisms in liquid phase. E1 is a two-step mechanism. The C–Cl bond is broken first and an intermediate carbonium ion is formed. The E2 or concerted mechanism is a one-step mechanism. Both bonds are broken at the same time. The mechanism found in a given system depends upon the relative strength of the interactions between reactant and catalyst as described above and in (*7*). If the influence of the electron pair acceptor site of the catalyst is high compared to that of the electron pair donor site, an E1 mechanism is to be expected. This is obviously so for X zeolites with bivalent cations. NaX with its certainly lower electron pair acceptor strength shows a high E2 character in the lower temperature range. As also observed earlier, the mechanism changes toward E1 with increasing temperature.

Over A zeolites, the E2 mechanism is preferred in the whole temperature range. This E2 mechanism is surprising with ZnA, since Zn^{2+} is generally found to be one of the most active cations. Following the explanation outlined above this must be interpreted as a lower influence of the cation in A than in X zeolites. As the nature of Zn^{2+} probably does not vary appreciably from one zeolite to the other, its lower activity may be ascribed to a "molecular sieve" effect (*20*), which means a lower accessibility. It may furthermore be assumed that the accessible Zn^{2+} ions in ZnA, which possibly should be localized at the "outer" surface, have a lower electric field than those in X cages.

Isobutene formation, which involves a skeletal isomerization, is clearly related to the E1 mechanism, i.e., to the capacity of the catalyst to produce carbonium ions. It is likely that carbonium ions are intermediates for all the products formed over E1 catalysts. This explains the equality of products obtained from 1- and 2-chlorobutane. The 1-butyl cation formed in the first step from 1-chlorobutane is immediately transformed to the 2-butyl cation which is more stable and which is formed from the 2-chlorobutane in the first step.



It is interesting to note now that this carbonium ion, which is formed in the first reaction step, is obviously not capable of being converted to isobutene. Isobutene is certainly a secondary product (see Fig. 4), which is formed in a second adsorption step from *n*-butene, especially from *trans*-2-butene. The conclusion may be drawn that the carbonium ions for formation of *n*- and isobutenes are different, but it is impossible at the moment to indicate the nature of this difference.

In former studies on dehydrohalogenation over salts and oxides, isobutene was not detected in appreciable amounts even over very active catalysts, which gave an E1 mechanism (*7, 9, 19*). The same was observed with butene isomerization (*22*). Once more this difference may be interpreted by the high activity of X zeolites compared with salts and oxides. On the other hand, isobutene formation has been reported in the cracking reactions of butylbenzene over silica–alumina at a temperature over 400°C (*21*) and in butene isomerization on alumina at 470°C (*27*).

ACKNOWLEDGMENTS

We are grateful to the Union Carbide Corporation for providing samples of zeolites.

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