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Product Distributions in the Dehydrochlorination of Some Chloroalkanes over Alumina, Silica–Alumina, and Potassium Hydroxide–Silica Gel

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Dehydrochlorination of five kinds of chloroalkanes which may give several isomeric products was investigated over alumina (A), silica–alumina (SA), and potassium hydroxide supported on silica gel (K–S) to discuss the characteristic properties of alumina in the elimination reactions. The product distributions from four chloroalkanes were well explained in terms of an E2 concerted mechanism on A, a carbonium ion mechanism on SA, and an E2 stepwise mechanism via a carbanion on K–S. *Trans* isomers were preferred slightly to *cis* isomers on K–S, whereas the *cis* isomers were predominant on A and SA, and especially the selectivity was very high on A. Stereospecific anti-eliminations were observable on A and K–S, although the reaction was nonstereospecific over SA. Poisoning effects of acetic acid and *n*-butylamine were studied on A and its active sites for the dehydrochlorination are discussed.

INTRODUCTION

Alumina has long been recognized as a useful catalyst in elimination reactions (*1*). Although it is very active in dehydration of ethanol (*2*), and in dehydrochlorinations of chloroethanes (*3*) and chlorohydrins (*4*), it has only small activity in dealkylation of alkylbenzene or esterification of ethanol and acetic acid (*5*). In contrast, silica–alumina has high activity in all these reactions (*2–4*). Furthermore, alumina has been reported to give a quite different selectivity in dehydrochlorination of 1,1,2-trichloroethane from that of silica–alumina (*3*).

Such catalytic activities of alumina may be assumed to be due to its binary sites of Lewis acidity and basicity (*2*a, c). By taking account of the rate-determining step, five kinds of mechanisms are conceivable in ionic eliminations (*6*). Among them, the reaction over A may follow an E2 concerted mechanism where the simultaneous cleavage of eliminating bonds is promoted by the binary sites, whereas silica–alumina may promote the carbonium ion mechanism.

In the present study, the dehydrochlorination of five chloroethanes has been investigated over alumina (A), silica–alumina (SA) and silica-supported KOH (K–S) in order to ascertain further the validity of the above assumptions. All the reactants used here are dehydrochlorinated into more than two kinds of corresponding olefins, so that the product distributions provide information on the reaction mechanism. Comparison of alumina with SA and K–S, which are typical solid acid and base, respectively, can clarify the catalytic characteristics of alumina. The *trans*/*cis* ratio of the formed olefins, the stereochemistry of elimination, and poisoning effects of *n*-butylamine and acetic acid are further investigated in order

TABLE 1

Product Distribution over Alumina

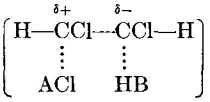
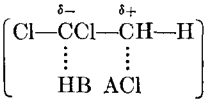
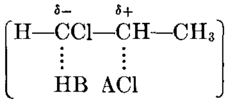
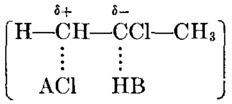
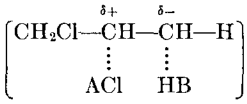
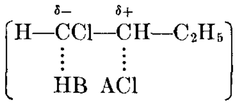
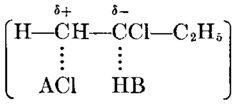
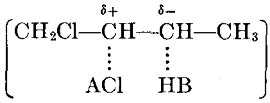
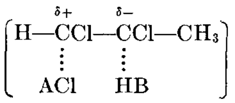
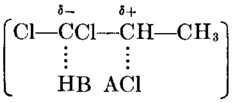
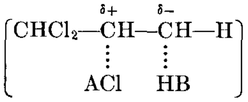
Reactant	Intermediate	Products	Selectivity (%)
TCE	 $\left[\begin{matrix}\mathrm{H{-}\overset{\delta+}{C}Cl{-}\overset{\delta-}{C}Cl{-}H}\\ \vdots\quad\vdots\\ \mathrm{ACl\quad HB}\end{matrix}\right]$	*cis*-$CHCl{=}CHCl$ *trans*-$CHCl{=}CHCl$	69.1 9.5
	 $\left[\begin{matrix}\mathrm{Cl{-}\overset{\delta-}{C}Cl{-}\overset{\delta+}{C}H{-}H}\\ \vdots\quad\vdots\\ \mathrm{HB\quad ACl}\end{matrix}\right]$	$CCl_2{=}CH_2$	21.4
DP	 $\left[\begin{matrix}\mathrm{H{-}\overset{\delta-}{C}Cl{-}\overset{\delta+}{C}H{-}CH_3}\\ \vdots\quad\vdots\\ \mathrm{HB\quad ACl}\end{matrix}\right]$	*cis*-$CHCl{=}CHCH_3$ *trans*-$CHCl{=}CHCH_3$	89.1 3.1
	 $\left[\begin{matrix}\mathrm{H{-}\overset{\delta+}{C}H{-}\overset{\delta-}{C}Cl{-}CH_3}\\ \vdots\quad\vdots\\ \mathrm{ACl\quad HB}\end{matrix}\right]$	$CH_2{=}CClCH_3$	2.6
	 $\left[\begin{matrix}\mathrm{CH_2Cl{-}\overset{\delta+}{C}H{-}\overset{\delta-}{C}H{-}H}\\ \vdots\quad\vdots\\ \mathrm{ACl\quad HB}\end{matrix}\right]$	$CH_2ClCH{=}CH_2$	5.1
DB	 $\left[\begin{matrix}\mathrm{H{-}\overset{\delta-}{C}Cl{-}\overset{\delta+}{C}H{-}C_2H_5}\\ \vdots\quad\vdots\\ \mathrm{HB\quad ACl}\end{matrix}\right]$	*cis*-$CHCl{=}CHC_2H_5$ *trans*-$CHCl{=}CHC_2H_5$	72.3 9.2
	 $\left[\begin{matrix}\mathrm{H{-}\overset{\delta+}{C}H{-}\overset{\delta-}{C}Cl{-}C_2H_5}\\ \vdots\quad\vdots\\ \mathrm{ACl\quad HB}\end{matrix}\right]$	$CH_2{=}CClC_2H_5$	3.5
	 $\left[\begin{matrix}\mathrm{CH_2Cl{-}\overset{\delta+}{C}H{-}\overset{\delta-}{C}H{-}CH_3}\\ \vdots\quad\vdots\\ \mathrm{ACl\quad HB}\end{matrix}\right]$	*cis*-$CH_2ClCH{=}CHCH_3$ *trans*-$CH_2ClCH{=}CHCH_3$	7.8 7.2
TCP	 $\left[\begin{matrix}\mathrm{H{-}\overset{\delta+}{C}Cl{-}\overset{\delta-}{C}Cl{-}CH_3}\\ \vdots\quad\vdots\\ \mathrm{ACl\quad HB}\end{matrix}\right]$	*cis*-$CHCl{=}CClCH_3$ *trans*-$CHCl{=}CClCH_3$	45.1 12.0
	 $\left[\begin{matrix}\mathrm{Cl{-}\overset{\delta-}{C}Cl{-}\overset{\delta+}{C}H{-}CH_3}\\ \vdots\quad\vdots\\ \mathrm{HB\quad ACl}\end{matrix}\right]$	$CCl_2{=}CHCH_3$	42.9
	 $\left[\begin{matrix}\mathrm{CHCl_2{-}\overset{\delta+}{C}H{-}\overset{\delta-}{C}H{-}H}\\ \vdots\quad\vdots\\ \mathrm{ACl\quad HB}\end{matrix}\right]$	$CHCl_2CH{=}CH_2$	Tr

TABLE 2

Product Distribution over Silica–Alumina

Reactant	Intermediate	Products	Selectivity (%)
TCE	$[\overset{+}{C}HClCH_2Cl]$	trans-$CHCl{=}CHCl$	14.4
		cis-$CHCl{=}CHCl$	85.6
	$[CHCl_2\overset{+}{C}H_2]$	$CCl_2{=}CH_2$	Tr
DP	$[CH_2Cl\overset{+}{C}HCH_3]$	trans-$CHCl{=}CHCH_3$	10.5
		cis-$CHCl{=}CHCH_3$	50.3
		$CH_2Cl{-}CH{=}CH_2$	39.2
	$[\overset{+}{C}H_2CHClCH_3]$	$CH_2{=}CCl{-}CH_3$	Tr
DB	$[CH_2Cl\underset{+}{C}HC_2H_5]$	trans-$CHCl{=}CHC_2H_5$	9.3
		cis-$CHCl{=}CHC_2H_5$	30.3
		cis-$CH_2ClCH{=}CHCH_3$	60.7
		trans-$CH_2ClCH{=}CHCH_3$	Tr
	$[\overset{+}{C}H_2CHClC_2H_5]$	$CH_2{=}CCl{-}C_2H_5$	Tr
TCP	$[\underset{+}{C}HClCHClCH_3]$	trans-$CHCl{=}CCl{-}CH_3$	46.4
		cis-$CHCl{=}CCl{-}CH_3$	53.5
	$[CHCl_2\underset{+}{C}HCH_3]$	$CCl_2{=}CHCH_3$	Tr
		$CHCl_2CH{=}CH_2$	Tr

to describe better the catalytic nature of alumina.

EXPERIMENTAL SECTION

Reagents. Haloalkanes obtained from Tokyo Kasei Co. were used without further purification. Meso- and *dl*-2,3-dichlorobutanes were separated from the commercial reagent (Tokyo Kasei Co.) by means of a gas chromatograph.

Catalysts. Silica–alumina (13% Al_2O_3), alumina [from $Al(NO_3)_3$] and KOH–SiO_2 were described in previous papers (*3–5*).

Apparatus and procedures. Elimination reactions were observed by means of microcatalytic gas chromatography with a column of tricresyl phosphate (4.7 m) at 60°C. All reactions were carried out at 300°C under a hydrogen gas flow at atmospheric pressure. No occurrence of elimination was observable over the glass wool packing, implying small contribution of simple pyrolysis. Catalytic activity and selectivity changed with successive pulses, so that the product distribution was observed for the first pulse. In the case of alumina, aluminum chloride seemed to be formed over the surface. Details on this subject will be presented in a separate paper. The elimination reaction was of first order under the experimental conditions, and the conversion was verified to be a linear function of the reciprocal space velocity (RSV) at low conversions. Thus, the slope of conversion/RSV gives the apparent rate constant, k (ml/g min). Poisoning effects of acetic acid and *n*-butylamine on the activity were observed after the elution which followed the pulse of 2 μl poison. Experimental details have been described in previous papers (*3–5*).

TABLE 3

Product Distribution over Potassium Hydroxide Supported on Silica Gel

Reactant	Intermediate	Products	Selectivity (%)
TCE	$[\overset{-}{\mathrm{C}}\mathrm{Cl_2CH_2Cl}]$	$\mathrm{CCl_2{=}CH_2}$	85.2
	$[\overset{-}{\mathrm{C}}\mathrm{Cl_2CH_2Cl}]$	*trans*-$\mathrm{CHCl{=}CHCl}$ *cis*-$\mathrm{CHCl{=}CHCl}$	8.8 6.0
DP	$[\overset{-}{\mathrm{C}}\mathrm{HClCClCH_3}]$	*trans*-$\mathrm{CHCl{=}CHCH_3}$ *cis*-$\mathrm{CHCl{=}CHCH_3}$	43.4 30.2
	$[\mathrm{CH_2Cl}\overset{-}{\mathrm{C}}\mathrm{ClCH_3}]$	$\mathrm{CH_2{=}CClCH_3}$	26.4
	$[\mathrm{CH_2ClCHCl}\overset{-}{\mathrm{C}}\mathrm{H_2}]$	$\mathrm{CH_2Cl{-}CHCl{=}CH_2}$	Tr
DB	$[\mathrm{CH_2Cl}\overset{-}{\mathrm{C}}\mathrm{ClCH_2CH_3}]$	$\mathrm{CH_2{=}CCl{-}C_2H_5}$	35.6
	$[\overset{-}{\mathrm{C}}\mathrm{HClCHClCH_2CH_3}]$	*trans*-$\mathrm{CHCl{=}CHC_2H_5}$ *cis*-$\mathrm{CHCl{=}CHC_2H_5}$	38.4 25.9
	$[\mathrm{CH_2ClCHCl}\overset{-}{\mathrm{C}}\mathrm{HCH_3}]$	$\mathrm{CH_2Cl{-}CH{=}CHCH_3}$	0
TCP	$[\overset{-}{\mathrm{C}}\mathrm{Cl_2CHClCH_3}]$	$\mathrm{CCl_2{=}CH{-}CH_3}$	91.7
	$[\mathrm{CHCl_2}\overset{-}{\mathrm{C}}\mathrm{ClCH_3}]$	*trans*-$\mathrm{CHCl{=}CClCH_3}$ *cis*-$\mathrm{CHCl{=}CClCH_3}$	5.5 2.8
	$[\mathrm{CHCl_2CHCl}\overset{-}{\mathrm{C}}\mathrm{H_2}]$	$\mathrm{CHCl_2{-}CH{=}CH_2}$	Tr

RESULTS

Product distributions of dehydrochlorination. Dehydrochlorination products of 1,1,2-trichloroethane (TCE), 1,2-dichloropropane (DP), 1,2-dichlorobutane (DB), and 1,1,2-trichloropropane (TCP) over alumina, SA and K–S are shown in Tables 1, 2 and 3, together with assumed intermediates which may explain the product distributions over these solids. As reported in previous papers (*3*, *6*), the carbonium ions and the carbanions are assumed in the stepwise elimination over SA and K–S, respectively, whereas a concerted mechanism where hydrogen and chlorine are simultaneously eliminated is assumed over alumina. To evaluate the stability of the intermediates of the ionic elimination, the stabilizing contributions of chlorine and methyl groups are summarized as follows: (a) α-Chlorine stabilizes the positive as well as the negative charge. (b) β-Chlorine stabilizes the negative charge, but destabilizes the positive charge. (c) Methyl group stabilizes the positive charge but destabilizes the negative one. These contributions are consistent with the resonance and inductive effects of the substituents. Product distributions shown in Tables 1, 2 and 3 are well understood in terms of the above criteria.

Stereoselectivities of dehydrochlorination. The reagents studied in the present work give the stereoselectivities of dehydrochlori-

TABLE 4

Trans/cis Selectivities of Olefin Formed in the Dehydrohalogenation

	A	SA	K–S	H_f (kcal/mole)	
				trans	*cis*
Dichloroethylene	0.14	0.17	1.50	−1.1[a]	−1.5[a]
1-Chloro-1-propene	0.07	0.21	1.44	−2.3[a]	−3.2[a]
1-Bromo-1-propene[b]	0.13	0.39	1.20	—	—
1-Chloro-1-butene	0.13	0.31	1.48	—	—
1,2-Dichloro-1-propene[c]	0.27	0.87	1.98	—	—

[a] Ref. (*13*).

[b] Taken from a previous paper (*6*).

[c] *Trans* and *cis* forms are distinguished by the relative location of chlorines.

nation which are shown in Table 4; some thermodynamic data are also shown. The *trans/cis* selectivities are quite different on these catalysts, implying different mechanisms over the catalysts. The *trans* isomers were formed preferentially over K–S, whereas *cis* isomers were preferred on A and SA; the high selectivity of *cis* formation over A should especially be noted.

Although thermodynamic data are not complete, the *cis* isomers of these chloroolefins may be more stable than the *trans*. Substituent effects on this selectivity are clearly noticeable over SA and slightly over A, but scarcely over K–S.

Stereochemistry of dehydrochlorination over A, SA, and K–S. The stereochemistry of elimination was studied over alumina, SA and K–S in order to discuss the origin of stereoselectivity as well as the reaction mechanism using *meso-* and *dl*-2,3-dichlorobutanes, although several works on this problem have been reported (*7*, *8*).

The results shown in Table 5 indicate that the eliminations over alumina and K–S were stereospecific reactions of the *anti* mode, where *cis*-2-chloro-2-butene from the *meso* form and *trans*-2-chloro-2-butene from the *dl* form were preferentially produced, although the stereospecificity was higher over K–S than over A. In contrast, no stereospecificity was obtained over SA, where the *trans* form was produced preferentially regardless of *meso-* or *dl*-2,3-dichlorobutane. Although nonstereospecificity on the acidic solid is consistent with the previous results (*7*, *8*), stereospecificity over alumina or K–S contradicts the results reported by

TABLE 5

Stereochemistry of Elimination

Reactants	Products	Selectivity (%)		
		A	SA	K–S
meso-2,3-Dichlorobutane	*cis*-$CH_3CH{=}CClCH_3$	79.0	21.3	92.8
	trans-$CH_3CH{=}CClCH_3$	21.0	73.8	7.2
	$CH_3CHClCH{=}CH_2$	Tr	4.9	Tr
dl-2,3-Dichlorobutane	*cis*-$CH_3CH{=}CClCH_3$	0	23.6	5.1
	trans-$CH_3CH{=}CClCH_3$	100	76.4	94.9
	$CH_3CHClCH{=}CH_2$	0	0	0

TABLE 6

Poisoning Effects of *n*-Butylamine and Acetic Acid on the Dehydrochlorination over Alumina

Poison	Elution time (min)	Catalyst (mg)	Conversion (%)	Product (conversion %)			
				1,1-DCE′	*trans* 1,2-DCE′	*cis* 1,2-DCE	1,1/1,2
None	—	51.1	29.0	7.6	2.6	18.1	0.3
CH_3COOH	22	53.1	9.6	3.4	0.9	5.3	0.5
	70	50.0	7.1	3.3	0.7	3.1	0.8
	75	51.1	4.3	2.7	0.4	1.2	1.7
	80	51.6	4.4	2.4	0.4	1.6	1.2
n-Butylamine	5	51.5	51.4	43.8	3.2	4.4	5.7
	91	50.0	50.3	34.5	5.2	10.6	2.2
	120	51.4	30.3	20.9	3.2	6.2	2.2

Noller *et al.* (*7*), but is consistent with those of Misono and Yoneda (*8*). The reason for this contradiction mentioned by Misono and Yoneda (*8*) may be correct.

Poisoning effects of basic and acidic substances on the activity of alumina. Poisoning effects of acetic acid and *n*-butylamine on the elimination activity of alumina are shown in Table 6. Nothing could be detected by gas chromatograph during the elution, indicating that the poisons may stay unchanged over the catalyst surface. Addition of acetic acid retarded the formation of 1,2-DCE (dichloroethylene) as well as 1,1-DCE. The recovery of 1,1-DCE formation was more rapid than that of 1,2-DCE formation as shown by the increased value of 1,1/1,2 ratio.

Addition of *n*-butylamine decreased the formation of 1,2-DCE very much, but increased that of 1,1-DCE as well as the total conversion. Adsorbed *n*-butylamine itself may accelerate the elimination reaction by its basicity. The total activity decreased with the period of elution, perhaps because of desorption of weakly adsorbed *n*-butylamine. Although the total activity fell to the level of fresh alumina after 120 min elution, 1,1-DCE was still formed preferentially.

DISCUSSION

Mechanism and stereoselectivity of dehydrochlorination reaction. Product distributions of dehydrochlorination observed in the present study are well explained in terms of the assumed mechanism and intermediates in the tables, indicating the validity of the assumptions. The stereochemistry and selectivity of these solids differed from each other, also suggesting different mechanisms for the dehydrochlorination over these solids.

The stereochemistry of the elimination reaction must be discussed in relation with the mechanism. The *anti*-elimination over alumina is consistent with an E2 concerted mechanism as often proposed in the homogeneous systems. In this mechanism, two active sites should be located to work simultaneously with the reactant. Such a situation may be possible in the pores of the solid catalyst (*9*). Misono and Yoneda (*8*) reported *anti*-elimination over a surface of small area without pores; however, cracks and defects of atomic order should be present enough to accelerate the *anti*-elimination.

It may be rather seldom that the specific *anti*-elimination is assumed in the stepwise elimination as observed over K–S in the present study. It may be possible when the reagent or the intermediate has a characteristic inclination for the stereospecific reaction such as the bridged-structure of the intermediate as often assumed for the radical and carbonium ion with bromine or iodine (*10*). Such an explanation has sometimes been postulated for the carbanions (*11*).

Another explanation of the anti-elimination in the stepwise reaction may be adsorption in a pore or a crack which may prohibit the rotation of the carbon–carbon bond of the carbanion during the stepwise reaction.

Trans/*cis* selectivity should be explained based on the above stereochemistry. The preferential formation of *trans* isomers may be due to the stability of the *trans* conformer of the starting reagent, because the reaction proceeds through an E2 stepwise mechanism where the elimination of a proton is rate-determining (Fig. 1). Thermodynamic data show that the *trans* conformer is more stable than the gauche one by 2.9 kcal/mole for 1,1,2-trichloroethane (*12*). The same trend may be expected for the homologues.

The intermediates over alumina should have a double bond nature to a considerable extent because proton and chlorine at the *trans* positions are to be eliminated simultaneously. The *cis* forms of intermediates seem to be stabler than the *trans* forms as some thermodynamic data of such olefins indicate (*13*), although the starting conformation leading to the *cis* form is less stable. These two postulates are compatible and may explain the high preference of the *cis* formation over alumina. An eclipsing effect (*14*) is usually considered to decrease the reactivity; however, it seems to accelerate the reaction in the present case.

A different explanation should be provided for the reaction over SA in spite of a similar preference for *cis* formation because the mechanism estimated differs and the *trans*/*cis* ratios are clearly larger than those of alumina. The reaction is stepwise and the carbon–carbon bond of the carbonium ion intermediate may rotate to be nonstereospecific over SA, although the intermediate of the bridged form may contribute to some extent (*6*). The *trans*/*cis* selectivity is determined by the reactivity of the leaving proton of the intermediate in the step which follows the formation of the intermediate (Fig. 2). The remaining large groups may be located far from the solid

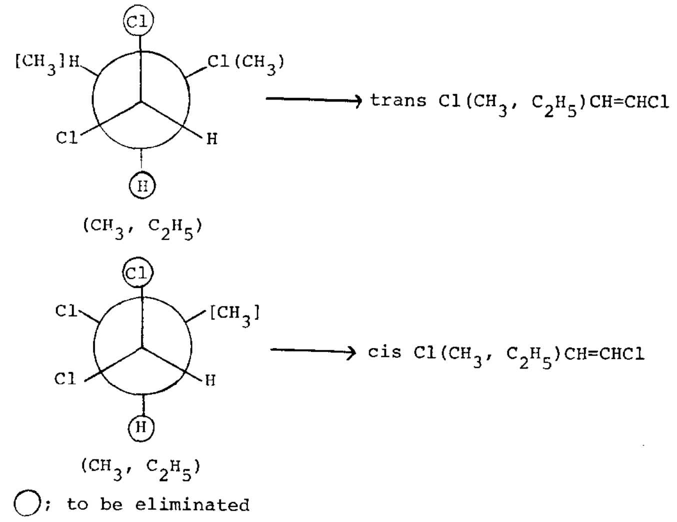


FIG. 1. Elimination over K–S.

surface, leading to preferential *cis* formation in the cases of TCE, DP and DB.

The situation is different in the case of TCP, for which the remaining methyl group is described by the brackets of Fig. 2. Two groups remaining on the intermediate from TCP may have similar size, resulting in the *trans/cis* ratio of near unity.

Active sites for dehydrochlorination. An acidic or basic site may interact with chlorine or a proton in the rate-determining step of the elimination over SA and K–S, respectively, this being consistent with their reaction mechanisms.

Cooperation of dual sites is a characteristic feature of alumina. This feature has been discussed for several reactions including dehydration (*2*a, c). Dehydrochlorination is one of these reactions so that there is an interesting common feature of δ_cLFER (*15*) in dehydration and dechlorination, whereas dealkylation and esterification show different behavior, as described previously (*5*). Dual sites of alumina are also indicated by the poisoning effect as well as product distribution, as shown in Table 6. Acidic as well as basic substances have effects on the dehydrochlorination over alumina, whereas only one of these substances has an effect over SA and K–S.

Although the chemical states of poisons over the catalyst surface could not be discussed precisely in the present study, they should have acid–base interaction with the active sites of the catalyst. Thus, the active site for the elimination reaction can be discussed. The retardation effect of acetic acid not only on the formation of 1,1-DCE but also on that of 1,2-DCE suggests its adsorption on the Lewis acid site of aluminum ion, since the acid site is considered to promote the formation of 1,2-DCE. Such adsorption has been proposed in the esterification over alumina (*5*). This adsorption seems to be very strong as indicated by the increasing 1,1/1,2 ratio with the time of elution. Coordination of acetate ion to the aluminum ion can occur on the surface of alumina.

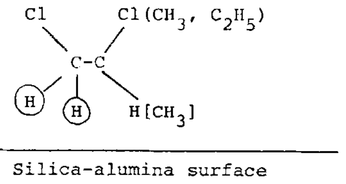


FIG. 2. Assumed intermediate over SA (hydrogens in the circles are leaving).

Decreased formation of 1,2-DCE by the adsorption of *n*-butylamine may support its formation over the acidic site. *n*-Butylamine adsorbed on the acidic site seems to be held strongly as shown by the slow recovery of the activity. In contrast, the weakly adsorbed *n*-butylamine may act as a base to promote the dehydrochlorination of TCE into 1,1-DCE, although it desorbs by elution after a certain period. Similar activity of the adsorbed amine was observed over the silica surface in spite of the more rapid desorption.

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