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The chemistry of alkyl dihalides in zeolite NaX at room temperature

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ABSTRACT

Alkyl dihalides adsorbed in NaX zeolite undergo room temperature, substitutional dehalogenation, single dehydrohalogenation, combined dehalogenation–dehydrohalogenation, or two consecutive dehydrohalogenations. The preference for a particular reaction depends on the nature and relative positions of the halogens, and on alkyl chain length. Nuclear magnetic resonance chemical shifts and mass spectrometric assignments to the reagents and products indicate the particular reactions taking place. All of the alkyl dihalides containing the iodo group (diiodoalkanes) studied ($\alpha\alpha$, $\alpha\beta$, α,γ) undergo only substitutional dehalogenation to form zeolite bound iodoalkoxy. The same chemistry was observed with both short and long chain diiodoalkanes. The dichloroalkane and dibromoalkane chemistry is dependent on the relative halogen positions and the alkyl chain length. The α,α dichloroalkanes and dibromoalkanes examined by us undergo single dehydrohalogenation, with the exception of 2,2-dichloropropane, which forms a mixture of dehydrohalogenation and substitutional dehalogenation products. The chemistry of α , β alkyl dihalides (Cl, Br) in NaX is dependent on the carbon chain length. The dihaloethanes (Cl, Br) undergo both substitutional dehalogenation and dehydrohalogenation. As the chain length increases to three carbon atoms or more, only dehydrohalogenation reactions take place. No alkyne products were observed with α , β dichloroalkanes and dibromoalkanes, an indication that NaX is too weak a base to initiate sequential dehydrohalogenations. The chemistry of α , γ dichloroalkanes and dibromoalkanes were also dependent on the chain length. The α , γ dihalopropanes (Cl, Br) in NaX form a propene–framework bound product, associated with dehydrohalogenation and subsequent substitutional dehalogenation. The α , γ dihalobutanes (Cl, Br) undergo two consecutive dehydrohalogenations to form dienes.

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1. Introduction

Dehalogenation of organic halides is an important research subject because of the increasing environmental accumulation of harmful organic halides, such as trichloroethylene (TCE), polychlorinated biphenyls, and chlorofluorocarbons [1]. Dehalogenation of these compounds has been achieved using a variety of media, including metal oxides, silicates, and zeolites [2–7]. For example, 1,2-dichloroethane undergoes dehydrochlorination thermally and catalytically to form vinyl chloride over silicates [2], aluminas, zeolites incorporating metals [3], and polyacrylonitrile-based carbon fibers [4]. Oxidatively, 1,2-dichloroethane yields CO₂, CO and HCl [5].

In a silica–alumina mixture, elimination reactions with 1,2- and 1,3-dichloropropane commences at 500 K to give three chloropropene isomers (3-chloropropene, *cis* 1-chloropropene, and *trans* 1-chloropropene) and HCl [6,7]. The major product (3-chloropropene) expected from 1,3-dichloropropane was only observed as a minor product, suggesting that a fast hydride shift occurs before deprotonation.

The compound 2,3-dichlorobutane forms diverse products (*cis*- and *trans*-2-chlorobutene, 2-chloro-1-butene, 1-3-butadiene, 1-butyne, and 2-butyne) on CaCl₂, CaO, and Al₂O₃ at temperatures between 150 and 370 °C [8]. Similar products are observed with 2,3-dibromobutane and 2,3-dichlorobutane adsorbed on MgO, CaO, SrO, Al₂O₃, [9], and silica gel (SiO₂), and on alkali salt-impregnated silica gels (KOH · SiO₂, K₂CO₃ · SiO₂) [10]. All of the examples above involve experiments conducted at temperatures higher than room temperature.

There are few reported studies of the reactions of alkyl halides in zeolites at room temperature. For example, the reductive dechlorination of α,ω -dichloroalkanes (1,4-dichlorobutane, 1,5-dichloropentane, and 1,6-dichlorohexane) adsorbed on NaX has been studied at room temperature [11]. Other reported room temperature studies include the reaction of 1,2- and 1,3-dichloropropane [6,7]. There are few room temperature reactions because of the difficulty in desorbing the decomposition products for analysis. For instance, in the dechlorination of α,ω -dichloroalkanes, the reaction was followed by determining chloride (Cl[−]) concentration, while the gas chromatographic mass spectrometric (GC-MS) technique was used with the 1,2- and 1,3-dichloropropane chemistry. The former method suffers severe disadvantages in that it cannot distinguish between dehydrohalogenation and

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dehalogenation, while the latter cannot be used to study framework-bound species.

NaX in its dehydrated form contains few Brønsted acid sites, except at defects. The room temperature chemistry discussed in this paper is stoichiometric chemistry with the zeolite, thus taking place in the zeolite cages. Therefore the chemistry described in this paper is almost entirely nucleophilic or basic chemistry at the supercage oxygen atoms. Hence, we do not address further the wealth of chemistry known to occur at acidic zeolite sites.

In our study, we used solid-state nuclear magnetic resonance (NMR) extensively. This technique is advantageous in that it is sensitive to (i) the products that are still embedded in the zeolite and to (ii) both olefins and framework species. Hence, in this way one can distinguish between dehalogenation and dehydrohalogenation.

2. Experimental

All of the alkyl dihalides were obtained from Sigma Aldrich in the highest grade available and were used, as received. Zeolite NaX was also obtained from Aldrich. The zeolite was dried by evacuation at 450 °C for 24 h, achieving an ultimate vacuum exceeding 1.2×10^{-5} torr. The alkyl dihalide adsorbates were taken through three freeze-pump-thaw cycles before adsorption into the zeolites by evaporative transfer. In the studies to be reported here, adsorbates were loaded at 3 molecules per supercage, unless otherwise stated. After adsorption, samples were left overnight at room temperature for equilibration.

For solution ^{13}C and ^1H NMR studies, the unreacted adsorbates with their reaction products were extracted from the zeolite using deuterated chloroform (CDCl_3) and analyzed using a Bruker AM 360 NMR spectrometer. A total of eight scans were performed for each solution, proton NMR experiment. Approximately 6000–10,000 scans were performed for each solution ^{13}C experiment. Powdered solid samples were measured with a Bruker AC 300 spectrometer, equipped with a Doty, 7 mm cross-polarization, magic angle spinning (CP MAS) probe. The CP MAS technique for ^{13}C was used as follows: After a 6.0 μs , $\pi/2$, high power, proton excitation pulse, cross polarization was achieved via a 2 ms contact time. The recycle delay was 3 s and the spinning rate was 4 kHz. For most solid-state ^{13}C MAS NMR runs, a total of 2048 scans were collected with chemical shifts adjusted to tetramethylsilane (TMS).

3. Results according to reaction type

3.1. Single substitutional dehalogenation

Dihalomethanes (Cl, Br and I) in NaX, undergo a single dehalogenation to form framework halomethoxy. As shown in the solid state spectrum of the reacted zeolite [Figure S1 of the Supplementary data](#), the broad peaks at 78, 80 and 81 ppm are assigned to framework chloromethoxy, bromomethoxy, and iodomethoxy respectively. At 3 molecules per supercage, residual dichloromethane, dibromomethane, and diiodomethane peaks appear at 57, 42 and 54 ppm, respectively. (As we have noted in a previous publication [12], chloroform solvent does not appear to undergo significant chemistry in the zeolite.)

No products were extracted from the zeolite loaded with diiodoalkanes. Only reactant peaks are observed in the CDCl_3 extracts of NaX exposed to 1,2-diiodoethane (3.6 ppm) [13], 1,3-diiodopropane (3.2, 2.2 ppm) [13], and 1,4-diiodobutane (3.1, 1.9 ppm) [13]. See [Figure S2 of the Supplementary data](#). Despite the absence of product(s) in the deuterated chloroform extracts, framework iodoalkoxy species are present in the reacted zeolites, as shown in the solid-state ^{13}C NMR spectra (see [Fig. 1](#)). We assign the broad

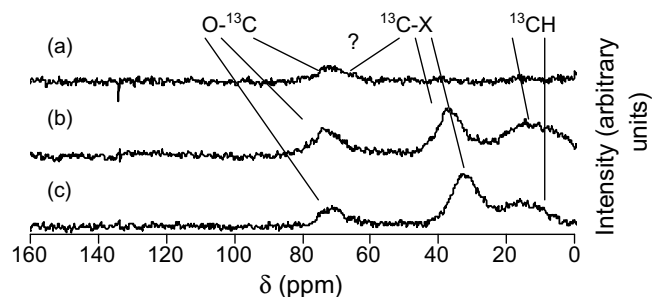


Fig. 1. Solid-state 75.4 MHz ^{13}C CP MAS NMR spectra of (a) 1,2-diiodoethane, (b) 1,3-diiodopropane, and (c) 1,4-diiodobutane exposed NaX. Spectra are offset for clarity. $\text{O}-^{13}\text{C}$ represents the iodoalkoxy ^{13}C atom attached to the framework O atom. $^{13}\text{C}-\text{X}$ represents the iodoalkoxy ^{13}C atom attached to the iodine atom. The $^{13}\text{C}\text{H}$ represents the non-iodine bearing and non-framework O atom bound ^{13}C atom.

peaks at 71 ppm, 74 ppm, and 73 ppm to the framework iodoethoxy, iodopropoxy, and iodobutoxy, respectively, based on similarities with other framework alkoxy species observed in previous work from our laboratory [14].

3.2. Mixed single substitutional dehalogenation and single dehydrohalogenation

Substitutional dehalogenation and dehydrohalogenation products in CDCl_3 extracts of the reactions of 1,2-dichloroethane and 1,2-dibromoethane in NaX appear in the spectrum of [Fig. 2](#) and those products remaining in the zeolite appear in the solid-state NMR spectrum of [Fig. 3](#).

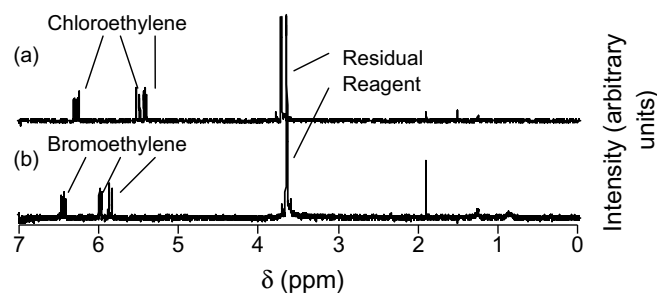


Fig. 2. Solution 360 MHz ^1H NMR spectra of the CDCl_3 extract of NaX exposed to (a) 1,2-dichloroethane and (b) 1,2-dibromoethane. Spectra are offset for clarity. The clipped off peaks at 3.7 ppm are the residual peaks.

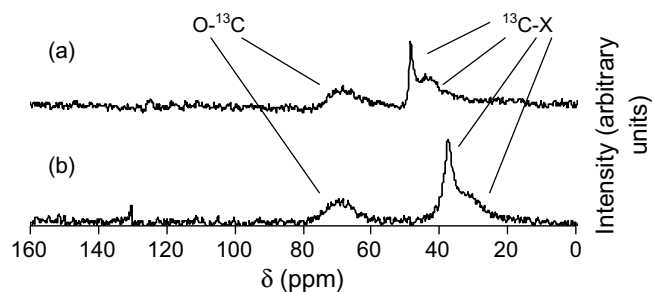


Fig. 3. Solid-state 75.4 MHz ^{13}C CP MAS NMR spectra of (a) 1,2-dichloroethane and (b) 1,2-dibromoethane exposed NaX. Spectra are offset for clarity. $\text{O}-^{13}\text{C}$ represents the haloethoxy ^{13}C atom attached to the framework O atom. $^{13}\text{C}-\text{X}$ represents the haloethoxy ^{13}C atom attached to the halogen atom (broad line) or the ^{13}C of residual 1,2-dihaloethane reagent (narrow line).

In Fig. 2, one can see that 1,2-dichloroethane and 1,2-dibromoethane form dehydrohalogenation products, chloroethylene (5.4, 5.5 and 6.3 ppm) [13] and bromoethylene (5.8, 6.0, 6.5 ppm) [13], respectively. Acetylene (2.1 ppm) [15], a product that would be obtained via two consecutive dehydrohalogenations, was not observed in either case. The peaks in the neighborhood of 3.6 ppm are associated with residual reactants.

Evidence of substitutional dehalogenation is found in Fig. 3. Both 1,2-dichloroethane and 1,2-dibromoethane undergo dehalogenation to form products that we assign to chloroethoxy (72 ppm) and bromoethoxy (69 ppm), respectively, based on our previous observations of framework alkoxy species [14].

3.3. Single dehydrohalogenation

3.3.1. Compounds with halogens in α,α positions (geminal dihalides)

Unlike 1,2-dichloroethane and 1,2-dibromoethane that react via substitutional dehalogenation and dehydrohalogenation (see Fig. 2 and Fig. 3), 1,1-dichloroethane undergoes single dehydrohalogenation only. Analogous chemistry is observed with the other geminal dihalides, 1,1-dichloropropane and 2,2-dichloropropane. See the spectra of the CDCl_3 extracts in Fig. 4 and of the species in the zeolite in Figure S3 of the Supplementary data. The dehydrohalogenation products obtained from 1,1-dichloroethane, 1,1-dichloropropane and 2,2-dichloropropane were assigned to 1-chloroethylene (117, 126 ppm), both *trans* 1-chloropropene (16, 117, 129 ppm) *cis* 1-chloropropene (12, 118, 126 ppm) [13] and 2-chloropropene (26, 112, 138 ppm), respectively [13].

The absence of the framework chloroalkoxy species (broad peaks in 60–75 ppm region) in the solid-state ^{13}C NMR spectra of the three adsorbates (Figure S3 of the Supplementary data) is evidence that the dehalogenation reaction is absent and that only one type of reaction (dehydrohalogenation) takes place. The olefinic peaks also appear in the solid-state spectrum of the zeolite loaded with 1,1-dichloroethane (118, 125 ppm), 1,1-dichloropropane (12, 16, 117, 118, 126, 129 ppm) and 2,2-dichloropropane (26, 112, 138 ppm).

The compounds 1,1-dibromoethane, 1,1-diiodoethane, 2,2-dibromopropane and 2,2-diiodopropane were not commercially available and no attempt was made to synthesize them for examination.

3.3.2. 1,2-Dihalopropanes

Single dehydrohalogenation chemistry was also observed with propanes containing the two halogens on adjacent carbon atoms (α, β position). Compound, 1,2-dichloropropane, reacted via dehydrohalogenation (see the CDCl_3 extract spectra in Fig. 5) to form *trans* 1-chloropropene (16, 117, 128 ppm) [13] and *cis* 1-chloropro-

pene (12, 119, 126 ppm) [13]. Similarly, 1,2-dibromopropane underwent a single dehydrohalogenation to form *trans* 1-bromo-1-propene (18, 104, 132 ppm) [13] and *cis* 1-bromo-1-propene (15, 108, 129 ppm) [13]. As earlier observed with the haloethanes, two consecutive dehydrohalogenations to form propyne did not occur. The peaks at 22, 49, 56 ppm in (a) and 24.3, 38.0, 46.0 ppm in (b) are associated with residual 1,2-dichloropropane and 1,2-dibromopropane, respectively [13]. Integration of the proton NMR spectra was done to determine the *cis/trans* ratio. Results showed that the *trans* product constituted about 71.5% and 72%, for 1,2-dichloropropane and 1,2-dibromopropane, respectively.

However, framework alkoxy (~ 70 ppm) was also observed with 1,2-dibromopropane, as evidenced by a weak peak in the solid-state spectrum of the zeolite in Figure S4 of the Supplementary data. This implies that dehalogenation and dehydrohalogenation may actually be competing processes, but the single dehydrohalogenation is strongly favored.

3.4. Loss of both halogens via a sequence of dehydrohalogenation and substitutional dehalogenation

Alkyl dihalides (Cl, Br) with the halogens attached at the α,γ positions undergo yet another mode of chemistry, different from that of the α, α or α,β alkyl dihalides (Cl, Br) presented in the previous sections. The results were surprising, because unlike in the previous sections, no products were obtained in the CDCl_3 extracts of 1,3-dichloropropane and 1,3-dibromopropane adsorbed on NaX (see Fig. 6). The ^1H NMR spectra of the extracts displayed only peaks associated with residual reactants, 1,3-dichloropropane (2.1, 3.6 ppm) and 1,3-dibromopropane (2.3, 3.5 ppm), respectively.

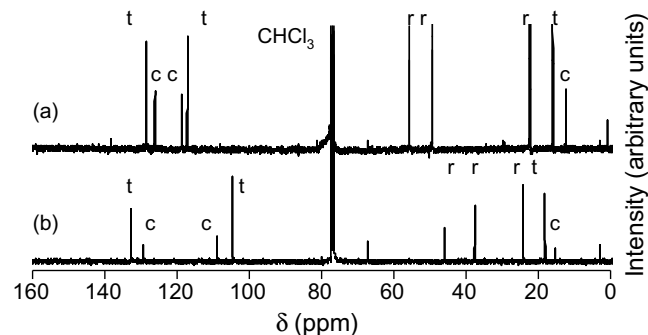


Fig. 5. Solution, 90.5 MHz, ^{13}C NMR spectra of the CDCl_3 extract of NaX exposed to (a) 1,2-dichloropropane and (b) 1,2-dibromopropane. Spectra are offset for clarity. The peak at 77 ppm is from the CHCl_3 impurity in the CDCl_3 solvent. Abbreviations c and t are for *cis*- and *trans*-1-halopropane products, respectively, and r is for residual reagent.

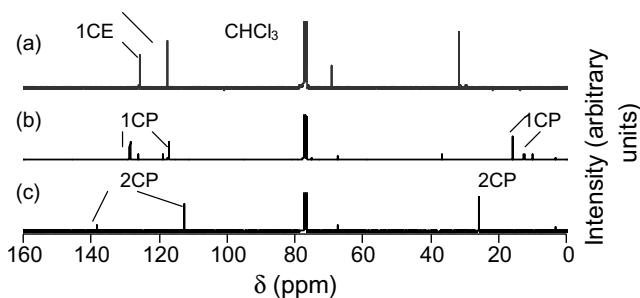


Fig. 4. Solution 90.5 MHz ^{13}C NMR spectra of the CDCl_3 extract of NaX exposed to (a) 1,1-dichloroethane, (b) 1,1-dichloropropane, and (c) 2,2-dichloropropane. Spectra are offset for clarity. The peak at 77 ppm (clipped off) is from CHCl_3 impurity in the CDCl_3 solvent. Abbreviations 1CE, 1CP, 2CP are for 1-chloroethylene, 1-chloropropene, and 2-chloropropene, respectively.

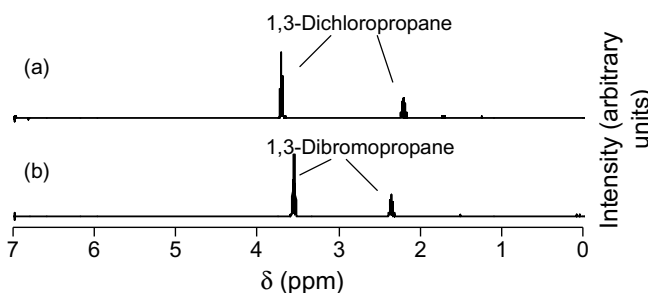


Fig. 6. Solution 360 MHz ^1H NMR spectra of the CDCl_3 extract of NaX exposed to (a) 1,3-dichloropropane and (b) 1,3-dibromopropane. Spectra are offset for clarity.

Despite the absence of products in the chloroform extracts, solid-state ^{13}C NMR spectra of the reacted zeolite (see Fig. 7) point to the presence of olefinic products (120, 134 ppm and 122, 134 ppm in Figs. 7a and b, respectively). Additionally, peaks associated with framework halopropoxy (70 ppm) are observed in Figs. 7a and b.

The results of Figs. 6 and 7 raised a puzzling question about our inability to extract the olefins using deuterated chloroform in this case. Preceding results (see previous Figures) and those in our earlier publication [14] show that olefins are generally easily extracted. These particular olefins are held tightly to the zeolite framework. Although framework alkoxy species are unaffected by chloroform, they are easily hydrolyzed by water to form alcohols [14]. In order to determine if the products were framework bound, equivalent amounts of water (3 per supercage) were evaporated into the zeolite already loaded and reacted with 1,3-dichloropropane. The mixture was then extracted with deuterated chloroform. Fig. 8 shows the solution ^{13}C NMR spectrum obtained from the extracts. Two products were identified, an allyl alcohol (64, 115, and 137) and 3-chloropropanol (33, 41, 60 ppm). The first two peaks of 3-chloropropanol (33, 41 ppm) coincide with that of the residual 1,3-dichloropropane [13].

Having examined the ^{13}C NMR, the two products, allyl alcohol and 3-chloropropanol in the extracts were further confirmed by examination with ^1H NMR. The multiplet peaks at 2.0, 2.2 and 3.6–3.7 ppm (Fig. 9) are associated with 3-chloropropanol. Peaks at 1.8, 4.1, 5.1, 5.3 and 5.9 ppm represent the allyl alcohol [13], while the peaks at 2.2 and 3.8 ppm are associated with residual 1,3-dichloropropane [13]. The formation of allyl alcohol implies that the original unhydrolyzed product was an olefin, bound to the zeolite by the framework alkoxy bond. This product will be proposed in Section 4 to occur via a dehydrohalogenation followed

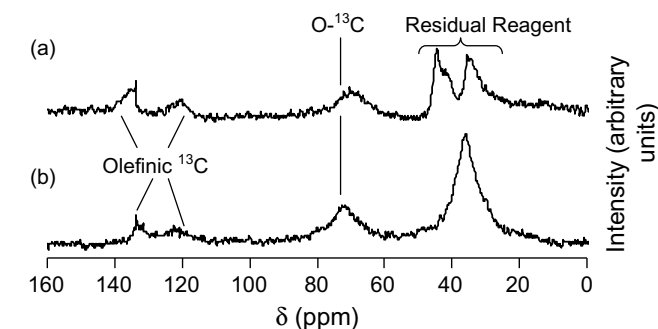


Fig. 7. Solid-state 75.4 MHz ^{13}C CP MAS NMR spectra of (a) 1,3-dichloropropane and (b) 1,3-dibromopropane exposed NaX. Spectra are offset for clarity. O- ^{13}C represents the propenoxy ^{13}C atom attached to the framework O atom.

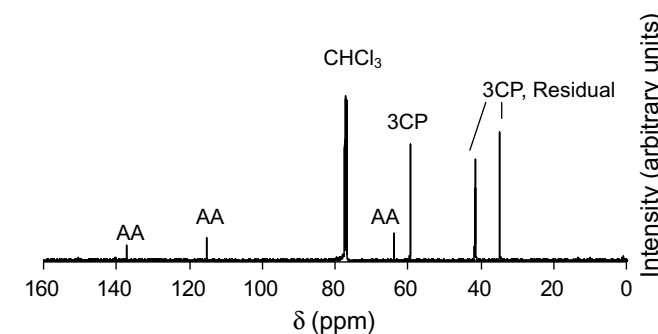


Fig. 8. Solution 90.5 MHz ^{13}C NMR spectrum of the CDCl_3 extract of 1,3-dichloropropane exposed NaX after addition of water. Abbreviations AA and 3CP represent allyl alcohol and 3-chloropropanol, respectively.

by substitutional dehalogenation, where the halogen at one end undergoes dehydrohalogenation and the halogen at the other end subsequently undergoes substitutional dehalogenation. The resulting dehalogenated carbon is then attached to the zeolite, as has been observed with other substitutional dehalogenation reactions, resulting in a framework alkenoxy species.

3.5. Loss of both halogens by consecutive dehydrohalogenations

Whereas we have seen that α,γ dihalopropanes (Cl, Br) undergo dehydrohalogenation and dehalogenation (Section 3.4), the series with longer chain length, α,γ dihalobutanes (Cl, Br) exhibit two consecutive dehydrohalogenations. In Fig. 10, showing the solution ^1H NMR spectra of the extracts after reaction of the 1,3-dihalobutanes (X = Cl, Br) with NaX, there is evidence for two consecutive dehydrohalogenation reactions to form 1,3-butadiene (5.0, 5.14, 6.3 ppm). Apparently, with 1,3-dichlorobutane, the reaction is incomplete, as evidenced by the presence of the additional, residual multiplet peaks centered at 2.1 ppm and 3.6 ppm [13], whereas the 1,3-dibromobutane exhibited no peaks from residual material. The absence of framework chlorobutoxy or bromobutoxy in the ^{13}C solid-state NMR spectra of the reacted zeolite in Figure S5 of the Supplemental data is an indication that the reaction takes place exclusively via dehydrohalogenation. The compounds, 1,3-diiodobutane was not commercially available and no attempt was made to synthesize them for study.

4. Discussion of the results

Alkyl dihalides in NaX zeolite undergo a rich variety of substitutional dehalogenation and dehydrohalogenation chemistries and

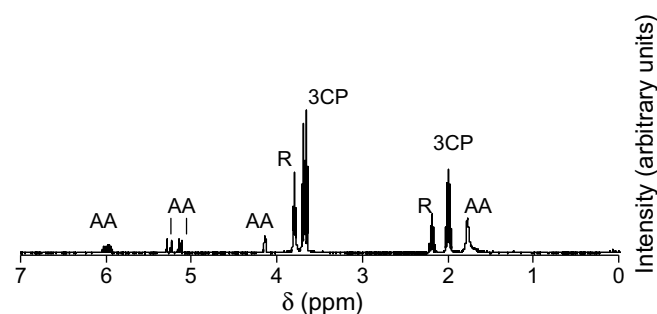


Fig. 9. Solution 360 MHz ^1H NMR spectra of the CDCl_3 extract of 1,3-dichloropropane exposed NaX after addition of water. Abbreviations AA, 3CP, and R represent allyl alcohol, 3-chloropropanol, and residual reagent, respectively.

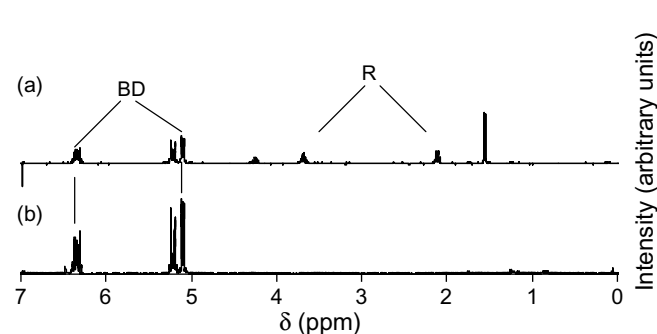


Fig. 10. Solution 360 MHz ^1H NMR spectra of the CDCl_3 extract of NaX exposed to (a) 1,3-dichlorobutane and (b) 1,3-dibromobutane. Spectra are offset for clarity. Abbreviations BD and R stand for butadiene and residual reagent, respectively.

mixtures and sequences thereof. The preference for a particular reaction is dependent on the type of halogen, the relative positions of the halogens, and the alkyl chain length. In some alkyl dihalide reactions with NaX, involving the loss of only one halogen, exclusively substitutional dehalogenation occurs, while in others exclusively dehydrohalogenation takes place. Other compounds lose a single halogen in a mixture of substitutional dehalogenation and dehydrohalogenation. Reactions of other alkyl dihalides with NaX exhibit the loss of two halogens in a sequence of two dehydrohalogenation reaction or in a sequence of dehydrohalogenations followed by substitutional dehalogenation. Dehydrohalogenation products include, in addition to the olefin, NaCl and an acid zeolite site, with no detectable HCl formation [14].

4.1. Influence of the particular halogen on the reaction

A comparison of the products obtained from chlorinated, brominated and iodinated compounds shows that iodinated compounds undergo substitutional dehalogenation only, while the bromo and the chloro compounds undergo dehydrohalogenation or both dehydrohalogenation and substitutional dehalogenation.

As discussed for monohaloalkanes [14], a C–X cleavage is fastest for iodide (X = I) and slowest for the fluoride. In liquid bases, the relative rates are about 30,000, 10,000, and 200 for iodides, bromides and chlorides, respectively [16]. The opposite trend applies to protons β to the halide; the most acidic protons (which cleave fastest) are those associated with the chlorides, while the least acidic are associated with iodides. The supercage oxygens of NaX are considered weakly basic (The basicity compares to 70% methanol [17]), but the Na^+ cations interact strongly with the halogens. Therefore the iodide cleaves more rapidly than the β -proton and forms the framework alkoxy. The C–I cleavage is comparatively faster in NaX zeolite than in liquid bases, because of the strong interaction between the iodide and the Na^+ counterions. The cleavage of the more acidic β -protons in the bromo and chloro compounds competes favorably with the halogen cleavage to give mixtures of olefins and framework alkoxy. The generalized substitutional dehalogenation reaction is shown in Scheme 1.

4.2. Influence of halogen position and carbon chain length on the reaction

Except for the iodinated compounds, any one of four types of reaction were found to occur, depending on the relative positions of the halogens and the alkyl chain length: (1) single dehydrohalogenation reaction, (2) mixed dehydrohalogenation and substitutional dehalogenation reactions, (3) two consecutive dehydrohalogenation reactions, or (4) a sequence of dehydrohalogenation reaction followed by a substitutional dehalogenation reaction.

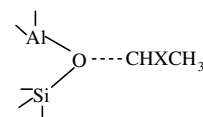
4.2.1. Alkyl dihalides with halogens in the α,α positions (geminal dihalides)

Geminal dihalides, such 1,1-dichloroethane, 1,1-dichloropropane, and 2,2-dichloropropane, undergo only the dehydrohalogen-

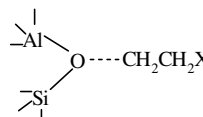
ation reaction (See Figure S2 of the Supplementary data). In general, the β -protons of geminal dihalides are very acidic due to their location next to two halogens (electron withdrawing), favoring dehydrohalogenation. Substitutional dehalogenation of geminal dihalides by zeolite NaX is disfavored because the resulting framework halolakoxy would have a halogen, an electron-withdrawing group, attached to the positively charged (electron deficient) carbon. This would make the framework species very unstable. In addition to the charge issue, the halogen being bulky would provide steric hindrance, making the positively charged carbon unable to approach the framework oxygen close enough for stabilization (Scheme 2). This hindrance was discussed in our previous paper [14].

4.2.2. Alkyl dihalides with halogens in the α, β positions

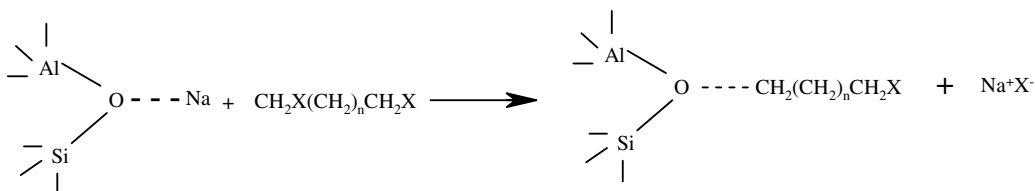
Depending on the carbon chain length, alkyl dihalides (X = Cl, Br) with the halogens in adjacent positions undergo dehydrohalogenation (see Fig. 4 and Figure S2 of the Supplementary data) or both dehydrohalogenation and substitutional dehalogenation (see Figs. 2 and 3). For shorter chains, such as 1,2-dichloroethane and 1,2-dibromoethane both reactions take place, but as one examines molecules with longer chains, dehydrohalogenation is favored. For molecules of shorter chain length, the stability of the substitutional dehalogenation product (framework alkoxy) from α, β alkyl dihalides is comparable to that of dehydrohalogenation (olefins) for two reasons. Firstly, since the halogen atom is in the adjacent position, the positively charged carbon is able to approach the framework oxygen more closely, leading to a stable 2-haloethoxy (see Scheme 3). Secondly, the framework alkoxy species with lower numbers of carbon atoms are more stable than those with larger numbers, making substitutional dehalogenation a competing process. The decreasing stability with increasing carbon atoms is because of the steric hindrance caused by the bulky alkyl substituents that prevents the framework oxygen from approaching the carbocation closely enough [14]. Thus as one progresses to the dihalopropanes, the stability of haloproxy (dehalogenation) decreases, favoring olefin formation (dehydrohalogenation).



Scheme 2. Hypothetical framework 1-haloethoxy obtained from 1,1-dihaloethane. The dangling bonds are to zeolite framework oxygens. X represents the halogen.



Scheme 3. Framework 2-chloroethoxy obtained from 1,2-dichloroethane. The dangling bonds are to zeolite framework oxygens. X represents the halogen.



Scheme 1. Proposed substitutional dehalogenation scheme for alkyl dihalides. The dangling bonds are to zeolite framework oxygens. X represents the halogen.

Despite 1,1-dichloropropane and 1,2-dichloropropane having different halogen positions, they form the same product, 1-chloropropene (See Figs. 4 and 5). The absence of 2-chloropropene peaks (26, 112, 138 ppm) in the washings of 1,2-dichloropropane implies the abstraction of the chlorine atom attached to the secondary carbon atom and not the abstraction of the chlorine atom attached to the primary one. This observation is consistent with our earlier results [14] showing a preference for abstraction of a halogen attached to a secondary carbon over a primary one. Although the elimination mechanism is E2, the transition state is more E1-like (with carbocation character) rather than synchronous E2 [14]. As a result, the transition state of a secondary alkyl halide is more stable than that of a primary one, leading to the abstraction of the halogen atom attached to the secondary C atom.

The absence of acetylene and allene (1,2-propadiene) in the dihaloethane and dihalopropane chemistries, respectively, is a result of the NaX zeolite being a weak base. It is known that haloalkenes are relatively unreactive, requiring a very strong base, such as NH_2^- , to undergo the second dehydrohalogenation step [16].

4.2.3. Alkyl dihalides with halogens in the α , γ positions

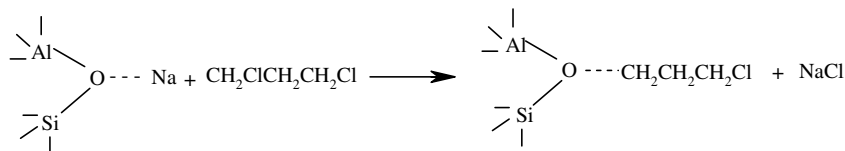
Alkyl dihalides with the halogens at α , γ positions undergo either substitutional dehalogenation followed by dehydrohalogenation or two consecutive dehydrohalogenation reactions, depending on the length of the carbon chain.

4.2.3.1. Propyl dihalides with halogens at α , γ positions. The results of Fig. 7 illustrate that 1,3-dichloropropane and 1,3-dibromopropane

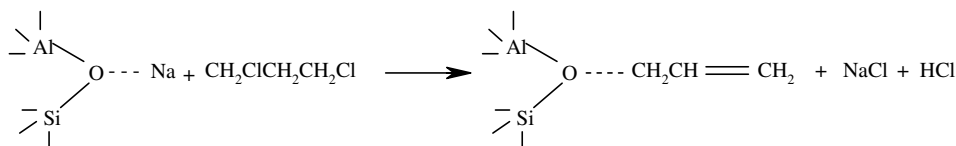
undergo two types of reactions: substitutional dehalogenation to form framework halopropoxy with loss of one halogen atom (see Scheme 4 for the example of 1,3-dichloropropane) and dehydrohalogenation followed by substitutional dehalogenation of the resulting halopropene to form a framework propeneoxy (see Scheme 5 for the example of 1,3-dichloropropane undergoing a two-step reaction via the proposed 1-chloro-2-propene intermediate.). In other words, one of the chain ends undergoes dehydrohalogenation and then the other end undergoes substitutional dehalogenation. The zeolitic oxygen then stabilizes the propene-carbocation formed.

The two framework species formed from these two types of reactions cannot be extracted from the zeolite using chloroform (see Fig. 6), because they are coordinatively bonded to the zeolite framework via the positively charged carbon. Chloroform does not wash framework species out of the zeolite, but water is capable of hydrolyzing the framework species to an alcohol [14]. Upon addition of water, framework chloropropoxy is observed to hydrolyze to 3-chloropropanol according to Scheme 6, whereas the propeneoxy is hydrolyzed to allyl alcohol according to Scheme 7.

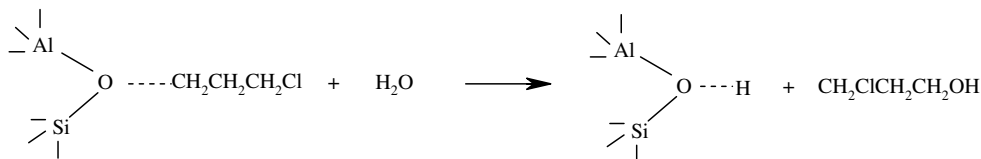
The 1-chloro-2-propene intermediate for the proposed sequence was not observed experimentally. However, an alternative concerted dehydrohalogenation–substitutional dehalogenation is unlikely because of framework–molecule steric constraints. It is likewise unlikely that the observed framework chloropropoxy species has the steric opportunity to line up with the framework so as alternatively to undergo a subsequent dehydrohalogenation, while also attached to the framework. Thus the proposed sequence with



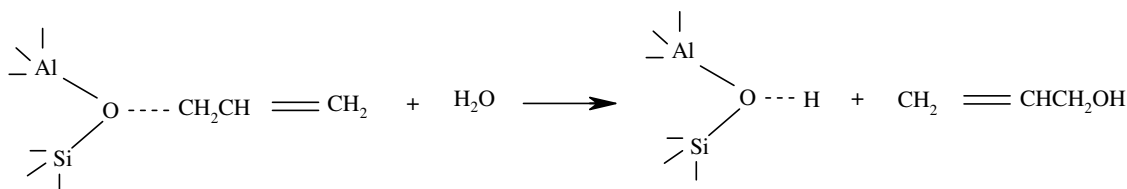
Scheme 4. Framework halopropoxy obtained from 1,3-dihalopropane. The dangling bonds are to zeolite framework oxygens.



Scheme 5. Observed framework propeneoxy obtained from 1,3-dihalopropane via the proposed 1-chloro-2-propene intermediate. The dangling bonds are to zeolite framework oxygens.



Scheme 6. Proposed framework chloropropoxy hydrolysis reaction. The dangling bonds are to zeolite framework oxygens.



Scheme 7. Proposed framework propeneoxy hydrolysis reaction. The dangling bonds are to zeolite framework oxygens.

the unobserved intermediate appears to be favored in view of the experimental evidence.

There is the possibility that some dehydrohalogenation of the 3-chloropropanol hydrolysis product occurs to give the allyl alcohol. However, the allyl alcohol still must also be the hydrolysis product of the observed framework bond olefin in view of the absence of any other product.

In summary two types of reactions take place. One of them stops after one substitutional dehalogenation step, due to the immobilization of the framework halopropoxy species. The other begins with dehydrohalogenation to a 1-halo-2-propene intermediate, followed by a substitutional dehalogenation step. The second step evidently can only be a substitutional dehalogenation, because another dehydrohalogenation would yield 1,2-propadiene, an unstable allene.

The possible nature of the interaction of an alkyl halide with the zeolite supercage surface preceding dehydrohalogenation has been discussed in connection with Scheme 2 of a previous publication [14]. We envisage more-or-less simultaneous supercage O atom-alkyl halide H atom and supercage Na ion-alkyl halide halogen atom interactions. Then products, NaCl, alkene, and acid zeolite site would appear to evolve smoothly with bond rearrangements. HCl is not formed in this process [14].

4.2.3.2. Butyl dihalides with halogens at α , γ positions. Consistent with our argument (Section 4.2.3.1.) concerning the prohibition of 1,2-propadiene formations, compounds with carbon chain of four carbon atoms apparently do permit formation of a diene. This is the case with the 1,3-dihalobutanes ($X = \text{Cl}, \text{Br}$), which both form 1,3-butadiene.

5. Conclusions

The NMR chemical shifts and GC-MS assignments to the various reagents and products in this study indicate that the chemistry of alkyl dihalides in NaX is dependent on the nature of the halogen, the relative positions of the halogens, and the alkyl chain length. All diiodoalkanes undergo dehalogenation to form framework iodoalkoxy. All other alkyl dihalides (Cl, Br) with the halogens at α , α and α,β positions undergo a single dehydrohalogenation, except for the α , β ethyl dihalides, where a mix of dehydrohalogenation and substitutional dehalogenation take place. With the halogens further apart at α,γ positions, two consecutive dehydrohalogenations occurs to form dienes. The only exception to this that we have observed in this limited study of chain length is the

α , γ alkyl dihalides with a carbon chain length of three carbon atoms, which display an intermediate behavior between single dehydrohalogenation and two consecutive dehydrohalogenations. In this case, the α , γ propyl dihalide forms framework propeneoxy, a product resulting from the consecutive reactions, dehydrohalogenation followed by a substitutional dehalogenation. The formation of dienes from α , γ propyl dihalides is inhibited by the instability of the resulting 1,2-propadiene. Two consecutive dehydrohalogenations to form alkynes is similarly not observed, because of the weak basicity of the NaX zeolite.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2008.06.005.

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