



# Multiple effects of the presence of water on the nucleophilic substitution reactions of NaX Faujasite zeolite with dimethyl methylphosphonate (DMMP)

Justin B. Sambur, David C. Doetschman \*, Szu-Wei Yang, Jürgen T. Schulte, Barry R. Jones, Jared B. DeCoste

Department of Chemistry, Binghamton University, Binghamton, NY 13902-6000, USA

Received 31 May 2007; received in revised form 14 September 2007; accepted 17 September 2007

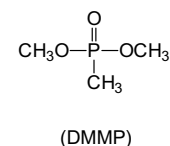
## Abstract

This study examines the dependence of the nucleophilic chemistry of dimethyl methylphosphonate (DMMP) adsorbed in NaX zeolite on adsorbed H<sub>2</sub>O content and on DMMP solution concentration. Primarily solid state and solution <sup>1</sup>H and <sup>31</sup>P NMR and GC–MS methods were employed. Experiments with H<sub>2</sub><sup>18</sup>O demonstrate that the nucleophilic attack in the zeolite is at the C atom of the ester group and not at the phosphonate P atom. Water is shown to play a complicated role in the chemistry at low water content by (1) facilitating DMMP adsorption to the supercage reaction sites and (2) hydrolyzing the ionic and framework-bound products of NaX nucleophilic attack on DMMP, but at higher water content (3) by inhibiting the chemistry, presumably through H-bonding to framework and ester O atoms and coordination of the stabilizing Na ions and (4) by exclusion of DMMP from the zeolite supercage volume at very high water adsorption. Evidence is presented for a deviation from an ideal DMMP adsorption dependence on DMMP concentration, when the presence of sufficient water for hydrolysis leads to a greater DMMP adsorption capacity in the zeolite. This is attributed to the release of DMMP binding sites in the zeolite supercage, when the strongly zeolite interacting framework-bound and ionic species are hydrolyzed. © 2007 Elsevier Inc. All rights reserved.

**Keywords:** Zeolite; Nucleophilic; Substitution; Phosphonate; Hydrolysis; Water; Adsorption; Clogging; H-bonding; Coordination

## 1. Introduction

Organophosphonates in solution are frequently used in agriculture as pesticides, insecticides, herbicides, and fungicides [1]. Additionally, organophosphonates comprise several classes of chemical warfare agents [2]. Dimethyl methylphosphonate (DMMP) (See structure 1) is used extensively as a type G and X simulant [3]. DMMP, commonly termed



an organophosphonate ester, exhibits similar structural and solubility properties to toxic organophosphonates. Yet it is experimentally useful, as it is considerably less toxic, less expensive, and readily available. The structure of DMMP mimics that of type G and X nerve agents, in regard to the methyl group directly bonded to the P atom of the P=O functional group.

Templeton and Weinberg [4] and some years later Mitchell et al. [5,6] studied the adsorption of three phosphonate esters, including DMMP, on metal oxide surfaces.

\* Corresponding author. Tel.: +1 607 777 2298; fax: +1 607 777 4478.  
E-mail address: ddoetsch@binghamton.edu (D.C. Doetschman).

The work shows close coordination of the processes of physisorption and chemical reactions involving hydrolysis. Their work reveals two types of nucleophilic chemistry, one with nucleophilic attack on the P atom and the other on the C atom of the ester functionality. A number of subsequent studies of NaX and NaY Faujasite zeolite chemistry with DMMP have also been made [7–9].

In cases of organophosphonate chemical spills or releases of nerve agents, any useful remediating agent dispersed on the hazardous area should exhibit the potential to neutralize all of the harmful substance. Residual hazardous materials may contaminate nearby water supplies or harm living beings in the surrounding area. It is therefore important to determine the organophosphonate neutralizing capacity of the remediating agent exposed to various amounts of water. The importance of this knowledge lies in having the ability to apply appropriate amounts of remediating agent to a hazardous location under ambient conditions. In this study, we examined the effects of water on the adsorption and chemical reaction of the DMMP simulant, upon contact with the model remediating agent, NaX Faujasite zeolite.

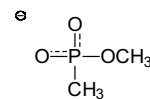
Experiments done with NaX in contact with DMMP in solution are admittedly less relevant to the remediation of nerve agents than NaX contact with the neat vapor, aerosol, or liquid agent normally dispersed. However, such solution experiments serve to bring DMMP into more uniform, homogeneous contact with the nanoporous NaX sample for the purpose of obtaining clear cut, fundamental research answers than can be devised with direct contact. Moreover, NaX contact with DMMP in solution is more relevant to the remediation of insecticides, pesticides, etc., which are commonly sold and used in solution.

In a previous publication on the nucleophilic reactions of Faujasite type zeolite NaX with dimethyl methylphosphonate (DMMP), [9] we revealed that water appeared to effect a balance between enabling and inhibiting effects on these reactions [10–13]. This was attributed to the mobilizing effects of water on the adsorption of DMMP into the zeolite and to the inhibition of the nucleophilic substitution chemistry by the presence of water in the zeolite.

In the aforementioned paper [9] and in papers on the nucleophilic chemistry of NaX with alkyl halides [14,15] our laboratory has established two key elements for this kind of chemistry. Firstly, the zeolite supercage O atoms near framework Al atoms are the nucleophiles capable of “attacking” electrophilic C atoms of substrate molecules adsorbed into the supercage. Secondly, cations located in supercage sites serve to assist the departure of leaving anions in the nucleophilic reactions. The latter makes certain zeolites, such as NaX, active in nucleophilic chemistry under ambient conditions, while others are relative inactive at room temperature. For example, NaY is inactive, while it has the same zeolite framework structure as NaX, but has a shortage of cations in the zeolite supercage cations sites [16–18].

In our previous work [9] we assigned the solid state  $^{31}\text{P}$  cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of DMMP,

which had been loaded into NaX, to the presence of anionic species II and III.

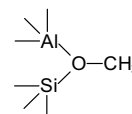


(II)



(III)

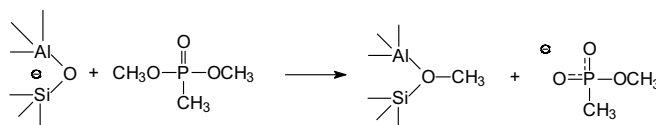
The assignments were made on the basis of solution  $^{31}\text{P}$  NMR studies of DMMP hydrolysis and on methylphosphonic acid (MPA) titration experiments. We also argued that the presence of the framework methoxy species (IV) was plausible, based on  $^{13}\text{C}$  CP



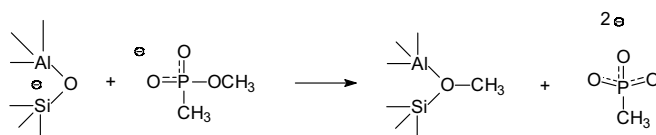
(IV)

MAS spectra of DMMP loaded NaX. This was taken to be evidence for the occurrence of the sequence of reactions in the absence of water, shown in Schemes 1 and 2. In these schemes and in the framework methoxy structure the dangling bonds are understood to be to other oxygens of the zeolite framework.

In this paper we present experiments that implicate water's role in the adsorption and reaction of DMMP in



Scheme 1. The nucleophilic reaction of the DMMP molecule with the zeolite supercage oxygen atom to form the framework alkoxy species (IV) and the singly ionic species (II).



Scheme 2. The nucleophilic reaction of the singly ionic species (II) with a second zeolite supercage oxygen atom to form another framework alkoxy species (IV) and the doubly ionic species (III).

NaX in several, not entirely surprising ways. NMR evidence is presented for a dynamic, competitive binding of water and DMMP that is discussed in terms of the ability of water to mobilize the diffusion of DMMP molecules within the zeolite. The degree and manner, with which DMMP reacts with NaX, and the degree and manner, with which products of the reaction are hydrolyzed by water, both exhibit a complex dependence on the DMMP and water content in the zeolite. NMR evidence is presented for the formation of the hydrolysis products of the anionic and framework methoxy products of the DMMP–NaX reaction in the presence of water. Adsorbed water, in the presence of excess DMMP, is shown to limit DMMP consumption in a manner suggesting a simple supercage volume exclusion by the presence of water. Below 3–4 DMMP molecules available per supercage, 3–4 molecules per supercage of water loaded into NaX do little to inhibit complete DMMP consumption. Studies with 3 and 4 molecules of adsorbed water per supercage show a non-monotonic dependence of the amount of DMMP consumed on the amount of DMMP made available. The observations are discussed in terms of the abilities of water (1) to mobilize DMMP diffusion in the zeolite, (2) to hydrolyze NaX–DMMP reaction products, (3) to quench the supercage O nucleophilicity through H-bonding of water to the O atom, (4) to quench Na ion leaving group assistance through water coordination around the Na ion, and (5) to prevent DMMP adsorption into the supercage by occupying some of its volume. Experiments were also undertaken to determine with more finality whether NaX nucleophilic attack on DMMP is at the P atom or the C atoms adjacent to the ester O atoms. Some of this work was presented in the defense of an honors thesis from this laboratory [19].

## 2. Experimental

Three types of experiments were done in this study. The first type was to determine whether zeolite nucleophilic attack is at the P atom of the DMMP P=O group or at the C atom of the DMMP methoxy groups by means of  $^{18}\text{O}$  labeling. The second type of experiment was a study of the dependence of DMMP adsorption and chemistry in NaX zeolite on NaX water content. The third type was a study of the dependence of DMMP degradation, as a function of DMMP loading into the zeolite at several different NaX water loading levels. Experimental details that are general to all three types of experiments are described first. We subsequently describe, individually, the experimental details relevant to each specific type of experiment.

### 2.1. General

DMMP, THF, and Na Faujasite zeolite were purchased from Sigma Aldrich. Deuterated chloroform was purchased from Cambridge Isotope Laboratories, Inc. All chemicals and solvents were purchased in the highest avail-

able grade and were used without further purification, except for the dehydration of NaX.

NaX was dried extensively. The NaX zeolite was evacuated to a pressure of  $2.4 \times 10^{-2}$  Torr in an approximately 2 cm. ID Pyrex tube at room temperature for 30 min. The temperature of the zeolite under vacuum was raised from room temperature in half-hour incremental steps to  $450^\circ\text{C}$  over a 3 h period. The samples were evacuated at  $450^\circ\text{C}$  for 8 h to a final pressure of  $4.8 \times 10^{-5}$  Torr in order to expel completely any  $\text{H}_2\text{O}$  from the zeolite. The resulting zeolite (Si/Al = 1.23) has been fully characterized according to methods described in several recent publications from our laboratory [9,14,15,20]. Calculated amounts of water, ranging from 1 to 30 molecules per supercage of NaX, were evaporatively transferred into the sample. The sample was left to equilibrate for one day at room temperature.

Desired amounts of DMMP were introduced into the zeolite via  $\text{CDCl}_3$  solvent. Approximately 3.0 g of the previously prepared samples of water loaded NaX were slowly added to 10 mL of  $\text{CDCl}_3$  in a 50 mL round bottom flask in an ice bath and stirred for 5 min. Then the mixture was warmed to room temperature and DMMP was added in the desired amount in relation to the number of NaX supercages in the sample. The mixture was refluxed for 6 h at  $40^\circ\text{C}$ . After refluxing, the mixture was centrifuged for 30 min at 7500 r.p.m. The  $\text{CDCl}_3$  portion was collected after centrifugation and the centrifugate was saved. Both were examined in subsequent NMR analyses. A  $\text{CDCl}_3$  slurry of DMMP and typical amounts of water were likewise refluxed in a control experiment in the absence of NaX.

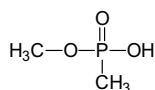
All  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  solution NMR spectra were recorded on a Bruker AM 360 NMR spectrometer. Ordinarily, a total of 64, 1000, and 400 scans were performed, respectively, for these experiments. Solid state  $^{13}\text{C}$  and  $^{31}\text{P}$  magic angle spinning (MAS) NMR spectra, the latter with and without  $^1\text{H}$ – $^{31}\text{P}$  cross-polarization (CP), were recorded on a Bruker AC 300 NMR spectrometer. The spinning rate for these experiments was 4 kHz. In the  $^{13}\text{C}$  and  $^{31}\text{P}$  CP MAS NMR experiments the contact times were 2 ms, and the recycle delays were 3 s and 5 s, respectively. Totals of 2048 and 512 scans were collected, respectively, with chemical shifts adjusted to external standards, tetramethylsilane (TMS) and 80%  $\text{H}_3\text{PO}_4$ , respectively.

### 2.2. DMMP position of nucleophilic attack

Water ( $\text{H}_2\text{O}$ ) enriched in  $^{18}\text{O}$  was purchased from Cambridge Isotope Laboratories, Inc. and was used without further purification.

NaX was dried, 4  $\text{H}_2^{18}\text{O}$  molecules per supercage of the zeolite were evaporatively transferred into the zeolite, and 10 DMMP per NaX supercage were subsequently transferred into the zeolite by refluxing in  $\text{CDCl}_3$ . The resulting slurry was centrifuged and the centrifugate was washed by stirring with THF. The resulting THF-zeolite slurry was centrifuged and the supernatant was examined with a Var-

ian 4000 GC–MS, equipped with a Varian Factor-Four VF-5 ms column. The column was programmed with a 3 min 50 °C post injection hold time, followed with a 10 °C/min ramp to 300 °C. It will be shown that a chemical procedure yields isolated methylphosphonic acid methyl ester (MPAME) (See structure V in Section 2) (and some residual



MPAME (V)

DMMP) in THF solution, whose isotopic content was then examined by MS.

### 2.3. Dependence on water content

NaX loaded with H<sub>2</sub>O in amounts 0–30 molecules per supercage was exposed to 1 molecule of DMMP per supercage of NaX by reflux in a CDCl<sub>3</sub> slurry and centrifuged. Solid state <sup>13</sup>C and <sup>31</sup>P CP MAS NMR spectra of the centrifugate samples were recorded. <sup>1</sup>H NMR spectra of the supernatant samples were also examined for the presence of residual DMMP and reaction products from the chemistry of DMMP, NaX, and H<sub>2</sub>O.

### 2.4. Dependence on DMMP loading

Methanol (CH<sub>3</sub>OH) and D<sub>2</sub>O were obtained from Sigma Aldrich in the highest grades available and used without further purification.

NaX was loaded with several different numbers of water per NaX supercage. The experiments with 3 or 4 molecules of water per supercage will be presented in detail. The samples were exposed to between 1 and 10 DMMP molecules per NaX supercage via refluxing in a CDCl<sub>3</sub> slurry. The samples were centrifuged, the centrifugate was examined with <sup>31</sup>P MAS NMR with and without CP, and the supernatant was examined with <sup>1</sup>H NMR for residual DMMP and reaction products. <sup>1</sup>H NMR spectra of the THF and D<sub>2</sub>O washes of one of the centrifugates were also examined. Methanol (CH<sub>3</sub>OH) was added to the <sup>1</sup>H NMR D<sub>2</sub>O wash sample and rerun in order to authenticate the presence of CH<sub>3</sub>OH. We also examined the solid state <sup>31</sup>P CP MAS NMR and the solution <sup>31</sup>P NMR spectra of the centrifugate and supernatant, respectively, from the THF wash of the original centrifugate described above.

## 3. Experimental results

Results of the three types of experiments are presented in the following sections.

### 3.1. DMMP position of nucleophilic attack

Injection of the THF wash, described in the Section 2, into the GC–MS led to a family of peaks whose main iso-

topes were  $m/z = 110.0$  (parent), 94.0, and 80.0 Dalton, eluting from the column at 77.5 °C with a  $1/e$  duration of 1.6 min. We assign this substance to MPAME (IV), the elution temperature of which is longer than the elution temperature 67.6 °C of the less polar and less H-bonding DMMP. By comparison of the maximum number of MS counts in the elution in the  $m/z$  ranges 109–111 and 111–113 Dalton, we estimate that no more than 3% of the <sup>18</sup>O from the hydrolyzing H<sub>2</sub><sup>18</sup>O exists in the MPAME. See following subsection.

### 3.2. Dependence on water content

In a previous publication from our laboratory, we described a qualitative examination of the <sup>31</sup>P CP MAS NMR spectra of NaX samples doped with varied amounts of water between 1 and 30 molecules per supercage that had been exposed to a CDCl<sub>3</sub> solution of 1 molecule of DMMP per NaX supercage [9]. In the present study we present a quantitative <sup>31</sup>P MAS NMR analysis without CP of the residual DMMP and the anionic products II and III, formed from the DMMP reaction with NaX. Further, we examine <sup>1</sup>H NMR spectra of the CDCl<sub>3</sub> solutions after contact with the water loaded NaX samples, for the purpose of examining the solutions for the presence of residual DMMP and DMMP chemical products. Finally, we present a <sup>13</sup>C CP MAS study of the NaX samples above, before and after a subsequent washing with THF, and with <sup>1</sup>H NMR of the THF solutions, in order to identify a hydrolysis product formed at higher DMMP levels.

In the published study of NaX samples doped with various amounts of water, the following conclusions had been drawn [9]. In NaX samples containing 0–3 molecules of water per supercage, into which DMMP was transferred by CDCl<sub>3</sub> solvent, the adsorbed DMMP exhibited substantial decomposition to form species assigned to anionic products II and III. Similar results were found when DMMP was evaporatively transferred into the zeolite, a challenge due to its low vapor pressure. At higher water loading levels than 3 molecules per supercage, the degree of DMMP decomposition dropped off with increasing water loading. The DMMP <sup>31</sup>P CP MAS spectrum also exhibited increasing signs of molecular mobility. However, this work was qualitative, due to the employment of cross-polarization, and focused on the NaX contents. Here we report on the examination of the contents that remain dissolved in the CDCl<sub>3</sub> transfer solvent, as a function of NaX water content, and on the quantitative examination of the proportions of DMMP and its anionic products in the NaX, as a function of water content.

We examined the <sup>1</sup>H NMR of the CDCl<sub>3</sub> supernatant from the centrifugation of the NaX, that had been loaded to various levels of H<sub>2</sub>O between 0 and 30 per supercage and in which 1 DMMP per supercage had been dissolved before refluxing and centrifugation. The NMR spectra revealed the presence of a small amount of the DMMP at NaX water loading levels of 0 and 1 H<sub>2</sub>O per NaX

327 supercage. However, at water levels of 3 H<sub>2</sub>O per NaX  
 328 supercage and above, no detectable DMMP remains in  
 329 the CDCl<sub>3</sub> solvent until around 30 H<sub>2</sub>O per supercage.  
 330 No DMMP chemical products are consistently present or  
 331 present above the CHCl<sub>3</sub> isotopic impurity level, although  
 332 traces of water are found sometimes at or above loading  
 333 levels of 3 H<sub>2</sub>O per supercage. The spectra may be exam-  
 334 ined in the [Supplementary data](#) for this paper. The amount  
 335 of residual DMMP in CDCl<sub>3</sub> after refluxing, when no  
 336 water was added to the NaX, was determined to be 0.6%  
 337 of the total DMMP added by comparison of the <sup>1</sup>H  
 338 NMR intensities with an authentic solution of DMMP of  
 339 known concentration.

340 From the <sup>31</sup>P MAS NMR spectra obtained without CP  
 341 we determined the percentages of DMMP (I), monoanionic  
 342 product (II), and dianionic product (III) present in NaX  
 343 doped with various water levels, to which DMMP was  
 344 transferred via CDCl<sub>3</sub> solvent containing 1 DMMP per  
 345 supercage. Peaks assigned to DMMP at 40 ppm, species  
 346 II at 28 ppm, and species III at 22 ppm [9] were integrated  
 347 and deconvoluted where necessary. See, for examples, spec-  
 348 tra in the following section on the dependence on DMMP  
 349 loading. The individual percentages and the percentage of  
 350 all DMMP decomposition products were calculated from  
 351 the integrals of the NMR peaks. The percentages are tab-  
 352 ulated in [Table 1](#) as a function of the water loading in NaX.

353 Surprisingly, no hydrolysis products, such as methyl-  
 354 phosphonic acid methyl ester (MPAME) (V) (at 32 ppm;  
 355 see the following section), were detected at this particular  
 356 DMMP loading level of 1 molecule per supercage at even  
 357 the highest of water loading levels.

### 3.3. Dependence on DMMP loading

359 In the experiments above with the introduction of 1  
 360 DMMP per supercage, we noted the absence of hydrolysis  
 361 products, such as MPAME (V) in the <sup>31</sup>P MAS NMR spec-  
 362 tra of the NaX, and the absence of other products, such as  
 363 methanol, in the <sup>1</sup>H NMR spectra of the CDCl<sub>3</sub> superna-  
 364 tant. Therefore we present firstly here an examination of  
 365 the <sup>31</sup>P MAS NMR spectra, with and without CP, of  
 366 NaX with water loading levels, known to give good  
 367 DMMP decomposition and adsorption, over a wide range  
 368 of DMMP CDCl<sub>3</sub> solution concentrations.

#### 3.3.1. Species identification

369 In [Fig. 1](#) are shown stacked plots of <sup>31</sup>P CP MAS NMR  
 370 spectra of NaX samples loaded with 4 H<sub>2</sub>O per supercage,  
 371 into which DMMP has been transferred from CDCl<sub>3</sub> solu-  
 372 tions of DMMP at concentrations of 1, 3, 4, 5, 6, 7, and 10  
 373 molecules per NaX supercage. In [Fig. 2](#) are shown the <sup>31</sup>P  
 374 MAS NMR spectra from a similar set of samples run with-  
 375

Table 1

Percentages of unreacted DMMP and individual ionic decomposition products, and the total percentage of the decomposition products formed when various numbers of water molecules had been introduced into the zeolite

H <sub>2</sub> O per NaX supercage	Percentage of DMMP	Percentage of methyl methylphosphonate anion <sup>-1</sup>	Percentage of methylphosphonate anion <sup>-2</sup>	Total percentage of decomposition products
0	22	67	11	78
1	18	57	25	82
3	37	3	60	63
10	76	15	9	24
30	97	3	0	3

Three molecules of DMMP per NaX supercage were introduced. The estimated uncertainty in the percentages was 0.9% and values are given to the nearest percent.

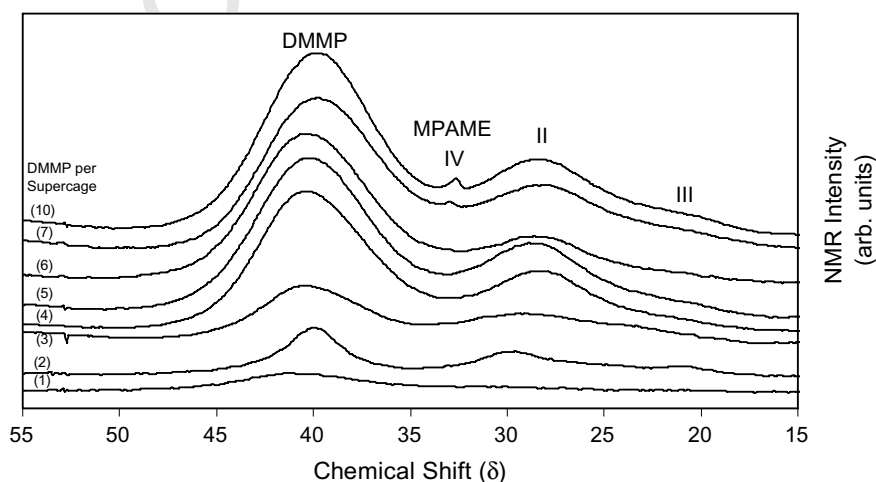


Fig. 1. Stacked plots of solid state <sup>31</sup>P NMR (MAS, 4 kHz) of NaX zeolite with <sup>1</sup>H-<sup>31</sup>P cross-polarization, loaded with 4 H<sub>2</sub>O per supercage, to which the indicated numbers of DMMP per supercage were added.

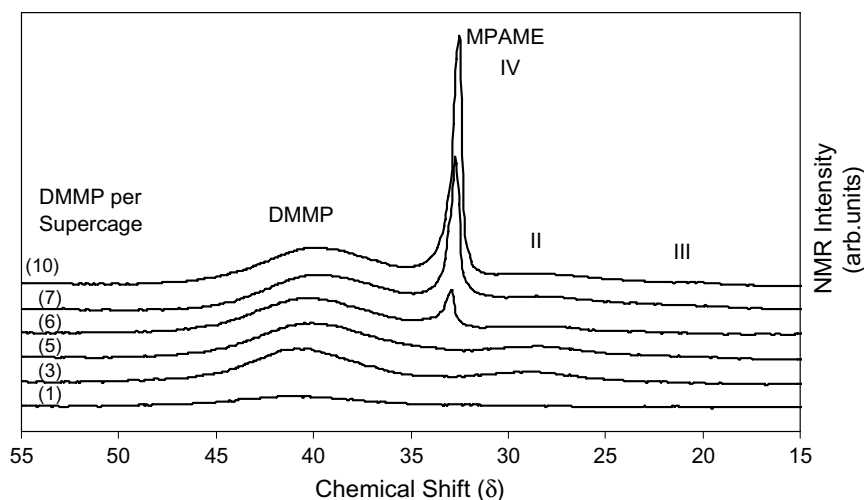


Fig. 2. Stacked plots of solid state  $^{31}\text{P}$  NMR (MAS, 4 kHz) of NaX zeolite without  $^1\text{H}$ - $^{31}\text{P}$  cross-polarization, loaded with 4  $\text{H}_2\text{O}$  per supercage, to which the indicated numbers of DMMP per supercage were added.

out cross-polarization (CP). DMMP (I), the anionic species (II) and (III), and MPAME (V) are assigned to the  $^{31}\text{P}$  NMR peaks, as indicated.

In the spectra of Fig. 2 there is the appearance of yet another relatively narrow peak at 32 ppm at DMMP solution concentrations above 5 molecules per supercage. This peak was not observed in the experiments at 1 DMMP per supercage, described in the previous section, and is relatively much less apparent in the CP experiments in Fig. 1. It is clear that the species responsible for the 32 ppm peak is much more highly motionally narrowed than the other species, suggesting a smaller species, such as the hydrolysis products MPAME (V) or methylphosphonic acid (MPA). MPA with a chemical shift of 29.2 ppm in  $\text{CDCl}_3$  solution [9] can be ruled out. The 32 ppm peak, however, is very close to the MPAME chemical shift of 32.6 ppm observed authentically in an aqueous solution hydrolysis of DMMP in  $\text{CDCl}_3$  [9]. A sample of NaX (4  $\text{H}_2\text{O}$  per supercage; 10 DMMP per supercage) exhibiting this peak was washed with THF. The  $^{31}\text{P}$  MAS NMR spectra of this sample, before and after washing, were compared with the  $^{31}\text{P}$  NMR spectrum of the THF wash solution. The spectra are shown in Fig. S1 of the Supplementary data. The results confirmed that the species giving the 32 ppm chemical shift had been removed and that the THF solution exhibits the peak at 32.6 ppm, characteristic of MPAME (V) [9]. The  $^1\text{H}$  NMR spectrum of the THF wash, shown in Fig. S2 of the Supplementary data, exhibits a methyl  $^1\text{H}$ - $^{31}\text{P}$  doublet at 0.076 ppm with a coupling constant of  $J(\text{P},\text{H}) = 17.22$  Hz. (The methyl  $^1\text{H}$  peak of the methyl ester appears to be obscured by the THF peaks.) The  $^1\text{H}$ - $^{31}\text{P}$  coupling constant of the authentic MPAME (V), present in DMMP solution phase hydrolysis in  $\text{CDCl}_3$ , is 17.21 Hz [9]. The results provide sound evidence for assigning the 32 ppm resonance in Figs. 1 and 2 and Fig. S1 Supplementary data to MPAME (V). It is noteworthy that there is no evidence, over the DMMP levels examined and at this range of water levels in NaX, for the

presence of the second hydrolysis product, MPA, a species whose chemical shift would be at about 29 ppm.

After washing with THF as described above and centrifuging, the centrifugate (from the 4  $\text{H}_2\text{O}$  and 10 DMMP per supercage sample) was further washed with  $\text{D}_2\text{O}$  and centrifuged. Fig. S3 of the Supplementary data shows the  $^1\text{H}$  NMR spectrum of the supernatant. The spectrum demonstrates the presence of DMMP (with the 2:1 ratio of  $J(\text{P}-\text{H})$  doublets) and MPAME (with the 1:1 ratio of  $J(\text{P}-\text{H})$  doublets). See Yang et al. [9] for the detailed assignments, chemical shifts, and coupling constants for DMMP and MPAME. THF and  $\text{H}_2\text{O}$  impurities can also be seen. In addition to these species, a methyl group peak at 3.12 ppm without coupling to  $^{31}\text{P}$  can be seen. Adding a drop of  $\text{CH}_3\text{OH}$  to the sample confirms the assignment of the peak to methanol by serving to increase the intensity of the 3.12 ppm peak, also shown in Fig. S3. The approximately equal integrated intensities of the MPAME and  $\text{CH}_3\text{OH}$  methyl group  $^1\text{H}$  NMR peaks are consistent with the 1:1 stoichiometry of MPAME and  $\text{CH}_3\text{OH}$  formation via DMMP hydrolysis, providing that comparatively small amounts of MPAME had been washed into the THF previously.

### 3.3.2. Variation with DMMP loading

The systematic variation in results was examined with 1–10 DMMP per NaX supercage at several water loading levels over a range that gives both significant DMMP adsorption from  $\text{CDCl}_3$  and significant DMMP chemical degradation. As a measure of the former, the residual DMMP in the  $\text{CDCl}_3$  supernatant was measured in terms of the intensity of the DMMP methyl  $^1\text{H}$  NMR peaks at 1.472 ppm, in comparison with the peaks in similar DMMP/ $\text{CDCl}_3$  solutions without contact with NaX. Examples of the results with 3 and 4  $\text{H}_2\text{O}$  per NaX supercage are shown in Fig. 3. These NMR intensity determinations were accurate to better than 100 intensity units. As a measure of the latter, the peaks of the  $^{31}\text{P}$  MAS NMR

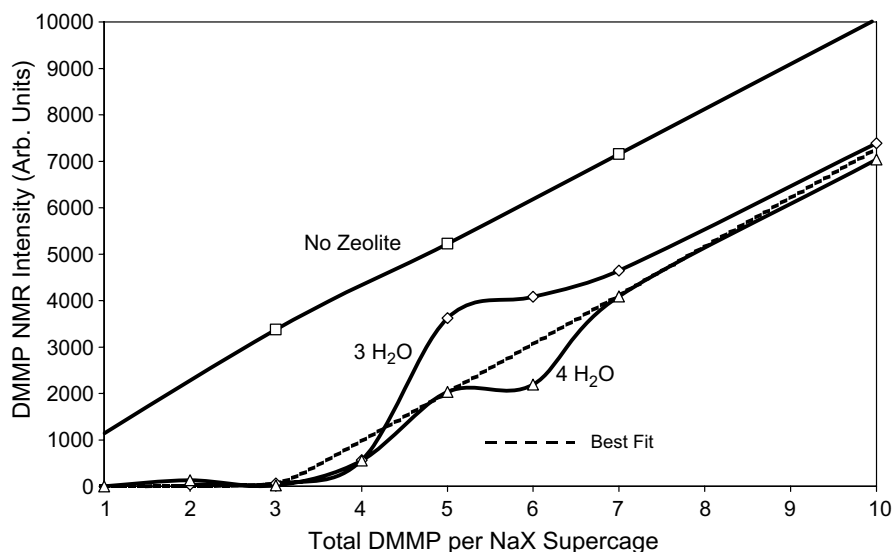


Fig. 3. NMR intensities of the residual DMMP in  $\text{CDCl}_3$  after the indicated amount of DMMP is brought into contact with a unit amount of NaX into which the indicated amounts of  $\text{H}_2\text{O}$  had been loaded (3  $\text{H}_2\text{O}$  and 4  $\text{H}_2\text{O}$ ). NMR intensities are accurate to better than 100 intensity units. These plots are compared with the NMR intensity of equivalent amounts of DMMP in  $\text{CDCl}_3$  that had not been contacted with NaX zeolite (No zeolite). A theoretical simulation (best fit) of the adsorption curve in the high and low DMMP regions of the observed data is shown for comparison in the dotted curve.

Table 2

Percentages of unreacted DMMP and individual decomposition products or groupings of them, and the total percentage of the decomposition products formed when various numbers of DMMP molecules had been introduced into the zeolite

DMMP per NaX supercage	Percentage of DMMP	Percentage of methyl methylphosphonate anion <sup>-1</sup> and MPAME	Percentage of methylphosphonate anion <sup>-2</sup>	Total percentage of decomposition products
1	90	10	0.00	10
2	77	16	7	23
3	78	22	0	22
5	71	26	3	29
6	46	54	0	54
7	23	64	13	77
10	13	83	4	87

Four molecules of  $\text{H}_2\text{O}$  per NaX supercage had been introduced in every case. The estimated uncertainties in the percentages range from 4.5% to much less than 1%. We present values here to the nearest percent.

spectra without cross-polarization of the centrifugate from the  $\text{CDCl}_3$  reflux, such as those in Fig. 1, were integrated. The percentage of DMMP, the sum of the percentages of singly anionic species II and MPAME, and the percentage of the doubly anionic species III, respectively, were calculated from the integrals and are given in Table 2 for the data obtained with 4  $\text{H}_2\text{O}$  per NaX supercage.

#### 4. Discussion of results

##### 4.1. DMMP position of nucleophilic attack

The GC–MS results on the MPAME removed by the THF washing from an NaX sample loaded with 4  $\text{H}_2^{18}\text{O}$  per supercage show no more than 3% of the MPAME to have taken up  $^{18}\text{O}$  from the loaded  $\text{H}_2^{18}\text{O}$ . In this sample 83% of the DMMP was converted to singly anionic species II or MPAME and 4% to the doubly anionic species III (See Table 2) Comparable amounts of species II and MPAME exist in the sample (See Figs. 1 and 2). Methanol is recovered in an approximately 1:1 stoichiometric amount with

MPAME (See Supplementary data). The presence of little or no  $^{18}\text{O}$  in MPAME from the water in the zeolite is consistent with a reaction, such as Scheme 1, in which the natural abundance of  $^{16}\text{O}$  remains on the MPAME precursor, species II. This is a pathway in which the nucleophilic attack occurs at the methyl C atom of the methyl ester group, displacing the methyl carbocation or forming IV.

All available evidence points to nucleophilic attack at the C atoms of the methyl groups of the ester functional groups. Supposing the nucleophilic attack to occur at the phosphonate P atom predicts outcomes that are contrary to experimental observations.

A fuller discussion of the discrimination of the experimental results and the logic leading to these conclusions is presented in the Supplementary data.

##### 4.2. Dependence on water content

In the study of residual DMMP after  $\text{CDCl}_3$  reflux, as a function of the amount of water loaded into the zeolite, less than 3  $\text{H}_2\text{O}$  per supercage leads to an appreciable amount

of DMMP in the  $\text{CDCl}_3$  (0.6% of the total DMMP). Three or more  $\text{H}_2\text{O}$  per supercage in the NaX results in undetectable residual DMMP, estimated to be  $\leq 0.1\%$  of total DMMP.

Also at  $\text{H}_2\text{O}$  loading levels of less than three per supercage, broadened powder pattern  $^{31}\text{P}$  CP MAS DMMP spectra with hints of spinning side band structure are observed, while at above 3  $\text{H}_2\text{O}$  per NaX supercage a progressively narrowed Lorentzian line is observed with increasing water loading level [9].

We take this to indicate that the highly mobile, [21–23] but more tightly bound, [24,25] water molecules begin to compete by the law of mass action at 3  $\text{H}_2\text{O}$  per supercage for DMMP binding sites in the zeolite at 1 DMMP per supercage.

At sufficiently high levels of  $\text{H}_2\text{O}$  one expects  $\text{H}_2\text{O}$  molecules to displace DMMP from the zeolite supercage altogether, because of supercage volume limitations.

We interpret the higher levels of residual DMMP found at water loading levels of less than three per supercage as a kinetic inhibition to the adsorption of DMMP into the zeolite supercages [26].

The following may be relevant to note. At or above 3  $\text{H}_2\text{O}$  per supercage, water is thought to mobilize DMMP, while at lower water loadings DMMP is less mobilized and there is evidence of its clogging the zeolite pores. If one can extend this logic to the mobilization of species II by water, one may be able to explain how species II and its  $\text{Na}^+$  partner can be moved more readily to another nucleophilic supercage O atom, where the subsequent reaction, Scheme 2, can occur.

Above 3 molecules of  $\text{H}_2\text{O}$  per supercage, there is a progressive drop in the percentage of II being formed and a progressive rise in unreacted DMMP. There is a small, perhaps significant rise in the percentage of species II at 10  $\text{H}_2\text{O}$  per supercage. Thus we hypothesize that the nucleophilic reactions are inhibited by  $\text{H}_2\text{O}$  by some or all of the following phenomena: (1) H-bonding to zeolite supercage nucleophilic O atoms, (2) coordination around supercage  $\text{Na}^+$ , and (3) H-bonding to the O atoms of the ester groups.

A fuller discussion of the discrimination of the experimental results and the logic leading to these conclusions is presented in the [Supplementary data](#).

#### 4.3. Dependence on DMMP loading

**Fig. 3** exhibits the linear relationship with near zero intercept between the DMMP  $^{13}\text{C}$  NMR intensity and the amount of DMMP dissolved in  $\text{CDCl}_3$  that is expected in the absence of zeolite (No zeolite curve). It is informative to compare with this calibration the NMR intensity of DMMP remaining in the  $\text{CDCl}_3$  after refluxing with NaX containing different amounts of water and after separating by centrifugation (3  $\text{H}_2\text{O}$  and 4  $\text{H}_2\text{O}$  curves). Also shown for comparison in **Fig. 3** is a simulation (best fit curve) of the high and low DMMP concentration limits based on the simple theory of adsorption. See the [Supplementary](#)

data for the derivation of the expression used. The parameters obtained from this simulation to the limiting behavior indicates effectively 3.1 DMMP binding sites per zeolite supercage and an equilibrium constant of 300 adsorbed DMMP molecules per residual DMMP molecule in solution at 0.3 g NaX per mL  $\text{CDCl}_3$  (See [Supplementary data](#)).

Firstly, note that above about 7 molecules of DMMP per NaX supercage an identical slope is observed but with displacements from the calibration curve. At 3  $\text{H}_2\text{O}$  per NaX supercage, the displacement corresponds to (an intercept of) about two adsorbed (and perhaps reacted) DMMP per supercage. At 4  $\text{H}_2\text{O}$  per supercage the intercept indicates a larger amount (2.5 molecules of DMMP per supercage) of adsorbed (and perhaps reacted) DMMP in the high DMMP limit. For want of physical reasons for more DMMP to be adsorbed with more  $\text{H}_2\text{O}$  in the zeolite, we take this to be evidence for more DMMP reacted with greater  $\text{H}_2\text{O}$  available. Evidence presented earlier in the previous section indicates that this chemistry is the hydrolysis of the singly ionic species II to form MPAME (See structure 5).

The behavior below 3 molecules of DMMP available per supercage is apparently independent of NaX water content and represents essentially complete adsorption of DMMP.

The intervening behavior observed between 4 and 7 molecules of available DMMP per NaX supercage is intriguing. With the sample of 3  $\text{H}_2\text{O}$  per supercage NaX, less DMMP is adsorbed (and perhaps reacted) in the NaX than would be predicted by the high DMMP limiting slope. The largest divergence appears at 5 available DMMP per supercage, whereas high concentration limiting behavior is being approached again at 6 DMMP per supercage. However, with 4  $\text{H}_2\text{O}$  per supercage of NaX, at 6 available DMMP per supercage a greater amount of DMMP is adsorbed (and perhaps reacted) than predicted by the high DMMP limiting slope. In general terms the observations appear to show that (a) with a less than critical amount of water, less than an expected amount of DMMP can be adsorbed (and perhaps reacted) in the NaX over an intermediate range of available DMMP and (b) with a more than critical amount of water, greater than an expected amount of DMMP can be adsorbed (and perhaps reacted) in the NaX over a similar intermediate range of available DMMP.

We offer a possible explanation for these observations. Namely one might expect the binding of further DMMP to be easier in the water-rich environment, while in the water-poor environment further DMMP binding might be relatively more inhibited.

A fuller discussion of the discrimination of the experimental results and the logic leading to these conclusions is presented in the [Supplementary data](#).

## 5. Conclusions

In summary, we have found that nucleophilic attack on DMMP in NaX zeolite occurs at the C atom of the ester

group and that water plays a complex role in this chemistry. Water may facilitate DMMP adsorption and hydrolysis at low water content, while inhibiting first the Na–DMMP chemistry and then DMMP adsorption, as the content increases. The DMMP hydrolysis appears to cause a deviation from ideal adsorption behavior.

These results point to the utility of a system with the excellent nucleophilic character of the NaX supercage oxygen atom and the appropriately juxtaposed counter ion, together with the ability of highly mobile adsorbed water to facilitate adsorption and hydrolysis. However, the study also points to difficulties with pore clogging phenomena and limited numbers of sites per supercage, even in this relatively large pore and large cage zeolite. The study suggests the need for a zeolite with similar characteristics and with very large pores and cages or a suitably dispersed nanoparticulate aluminosilicate, in order to adsorb and neutralize organophosphonate toxins efficiently. Such dispersion might be achieved by tethering the nanoparticles to an open polymeric or dextrimeric structure.

### Acknowledgments

We acknowledge the support of this work by the US Army Research Office through Grant W911NF-07-1-0042, a Grant (#4355) from the Institute of Hazardous Materials Management, and the Binghamton University College of Arts and Sciences.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.micromeso.2007.09.018](https://doi.org/10.1016/j.micromeso.2007.09.018).

### References

- [1] L. Karalliedde, S. Feldman, J. Henry, T. Marrs (Eds.), *Organophosphonates and Health*, Imperial College Press, London, 2001.

- [2] *Medical Management of Chemical Casualties Handbook*. U.S. Army, Medical Research Institutes of Chemical Defense, Aberdeen Proving Ground, Maryland, 1995.
- [3] S.L. Hoening (Ed.), *Handbook of Chemical Warfare and Bioterrorism*, Greenwood Press, Westport, Connecticut, 2002.
- [4] M.K. Templeton, W.H. Weinberg, *J. Am. Chem. Soc.* 107 (1985) 97.
- [5] M.B. Mitchell, V.N. Sheinker, E.A. Mintz, *J. Phys. Chem. B* 101 (1997) 11192.
- [6] V.N. Sheinker, M.B. Mitchell, *Chem. Mater.* 14 (2002) 1257.
- [7] G.W. Wagner, P.W. Bartram, *Langmuir* 15 (1999) 8113.
- [8] K. Knagge, M. Johnson, V.H. Grassian, S.C. Larsen, *Langmuir* 22 (2006) 11077.
- [9] S.-W. Yang, D.C. Doetschman, J.T. Schulte, J.B. Sambur, C.W. Kanyi, J.D. Fox, C.O. Kowenje, B.R. Jones, N.D. Sherma, *Micropor. Mesopor. Mater.* 92 (2006) 56.
- [10] Z. Zhang, N.J. Turro, L. Johnston, V. Ramamurthy, *Tetrahedron Lett.* 37 (1996) 861.
- [11] W. Ortiz, F.L. Cozens, N.P. Schepp, *Org. Lett.* 1 (1999) 531.
- [12] K. Shirono, A. Endo, H. Daiguji, *J. Phys. Chem. B* 109 (2005) 3446.
- [13] E.H. Ellison, *J. Phys. Chem. B* 103 (1999) 9314.
- [14] C.W. Kanyi, D.C. Doetschman, J.T. Schulte, K. Yan, R.E. Wilson, B.R. Jones, C.O. Kowenje, S.-W. Yang, *Micropor. Mesopor. Mater.* 92 (2006) 292.
- [15] C.W. Kanyi, D.C. Doetschman, S.-W. Yang, J.T. Schulte, B.R. Jones, *Micropor. Mesopor. Mater.*, in press.
- [16] D. Breck (Ed.), *Zeolite Molecular Sieves*, John Wiley & Sons, NY, 1974.
- [17] D.H. Olson, *Zeolites* 15 (1995) 439.
- [18] C. Baercher, W.M. Meier, D.H. Olson (Eds.), *Atlas of Zeolite Framework Types*, The Commission of the International Zeolite Association, 2001.
- [19] J. Sambur, *Decomposition of Dimethyl Methylphosphonate (DMMP) in Sodium-X Type Faujasite Zeolite*, Honors Thesis, State University of New York at Binghamton, Binghamton, NY, 2006.
- [20] J.D. Fox, A. Meenakshi, *J. Phys. Chem. B* 109 (2005) 9917.
- [21] P. Pissis, D. Daoukaki-Diamanti, *J. Phys. Chem. Solids* 54 (1993) 701.
- [22] N. Cvjeticanin, S. Mentus, N. Petranovi, *Solid State Ion.* 47 (1991) 111.
- [23] L. Broussard, D.P. Shoemaker, *J. Am. Chem. Soc.* 82 (1960) 1041.
- [24] C.E.A. Kirschhock, B. Hunger, J. Martens, P.A. Jacobs, *J. Phys. Chem. B* 104 (2000) 439.
- [25] F.M. Higgins, N.H. de Leeuw, S.C. Parker, *J. Mater. Chem.* 12 (2002) 124.
- [26] M.C. Mittelmeijer-Hazeleger, A.F.P. Ferreira, A. Blik, *Langmuir* 18 (2002) 9613.

631  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641  
642  
643  
644  
645  
646  
647  
648  
649  
650  
651  
652  
653  
654  
Q1 655  
656  
657  
658  
659  
660  
661  
662  
663  
664  
665  
666  
667  
668  
669  
670  
671  
672  
673  
674  
675  
676  
677