

Sodium X-type faujasite zeolite decomposition of dimethyl methylphosphonate (DMMP) to methylphosphonate: Nucleophilic zeolite reactions I

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Abstract

Dimethyl methylphosphonate (DMMP), used extensively as a nerve agent simulant, strongly adsorbs in X-type faujasite zeolite and undergoes nucleophilic substitution by the supercage oxygens. Solid state magic angle spinning (MAS) ^{31}P and cross polarization (CP) MAS ^{13}C NMR studies of the zeolite were performed after adsorption of DMMP into it. Methylphosphonate ions and possibly a framework methyl species are formed at low levels of water. The greater reactivity of NaX than the reactivity of NaY toward VX (phosphonothioic acid, methyl-, *S*-[2-[bis(1-methylethyl)amino]ethyl] *O*-ethyl ester) and one of its simulants [G.W. Wagner, P.W. Bartram, *Langmuir* 15 (1999) 8113], may be attributable to the smaller Si:Al ratio of NaX. Consequently, the NaX framework oxygen atoms are more nucleophilic and supercage Na ions are present to attract the methylphosphonate ion leaving groups.
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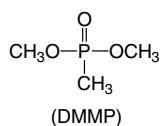
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1. Introduction

Dimethyl methylphosphonate (DMMP) has been used extensively as a type G and type X nerve agent simulant because of the common presence of alkoxy substitution at the P atom (Structure 1). The G- and X-type nerve agents, as well as methods to adsorb and decompose them chemically, continue to be of national security interest because of the needs to detect and decontaminate affected areas and populations. There also continues to be interest in the detection, decontamination, and destruction of chemical weapons. Zeolites have been of interest because of their generally high adsorptivities and their catalytic potential. Combining zeolite adsorbency with potential

chemical reactivity has been examined previously [1] in a study of NaY (and AgY) zeolite activity against VX and one of its simulants, *O*, *S*-diethyl phenylphosphonothiolate (DEPPT). The study did not show a major destruction of these compounds, and, consequently, the present study focuses mainly on the X-type zeolite NaX. Nevertheless, the interactions and reactions of alkyl phosphonates with various Al, Si, and other oxides continues to be of interest [2–5]. Common to these studies are (a) the interactions of the phosphonates with the oxygen atoms or the Brønsted acid –OH surface groups of these materials and (b) nucleophilic substitution into the alkyl phosphonate, the most common example of which is hydrolysis in the presence of water or –OH groups. The objectives of this study are to determine the extent of DMMP adsorption and to determine the extent and chemistry of its decomposition in the X-type zeolite. NaX and NaY zeolites were studied.

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Structure 1.

2. Experimental

A brief description of the experimental procedures employed in this work follows. Details about the materials, chemicals, characterization, and procedures are given in the [supporting information](http://www.sciencedirect.com), which is available at <http://www.sciencedirect.com>.

The NaX and NaY were dried by evacuation at 450 °C. The zeolite was characterized in several ways [6,7]. Specified amounts of water, measured by weighing, were also added by evaporative transfer to the dried NaX up to 30 molecules per supercage. Thermogravimetric analysis (TGA) characterization of the water-loaded zeolite showed a good linear correlation of TGA response with weight of loaded water. Subsequently, DMMP was evaporatively added at one molecule per supercage to a dry NaX or NaY sample and DMMP was also loaded at one molecule per supercage into the range of H₂O loaded samples via a slurry with CDCl₃. After the DMMP loading into NaX or NaY via CDCl₃ was complete, the CDCl₃ supernatant from centrifugation was saved for NMR analysis. The loaded zeolite centrifugate was washed with THF and the washings were likewise centrifuged and saved for solution NMR analysis. The washed centrifugate was also saved

for solid state NMR analysis and was characterized by IR (see [supporting information](#)).

In order to obtain NMR reference spectra, DMMP was subjected to acid hydrolysis and the equilibrium mixture was analyzed by solution NMR, thereby synthesizing and identifying the chemical shifts of the first hydrolysis product. Likewise, methylphosphonic acid (MPA) was titrated with NaOH to the first and second equivalence points and solution NMR reference spectra of each were recorded, thereby synthesizing and identifying the chemical shifts of the first and second methylphosphonate ions in solution. Solution ³¹P NMR spectra were recorded and referenced to PCl₅ at −80 ppm. Solution ¹H and ¹³C NMR spectra were recorded relative to tetramethylsilane (TMS) at 0 ppm.

2.1. Acid hydrolysis of DMMP

DMMP (5 mmol) and 0.35 mL of 35% DCl in 2 mL D₂O were placed in a 50 mL round bottom flask with 18 mL of CDCl₃. The two-phase mixture was stirred overnight at 60 °C.

In [Fig. 1](#) is shown the 2D ³¹P–¹H solution NMR spectrum of the DMMP hydrolysis equilibrium mixture in D₂O. DMMP exhibits a ³¹P chemical shift of 36.8 ppm, an α-methyl ¹H with δ = 1.2005 ppm and ³¹P splitting of 0.05 ppm, and a methoxy ¹H with δ = 3.35 ppm and ³¹P splitting of 0.05 ppm. The first hydrolysis product exhibits a ³¹P intensity approximately twice that of DMMP with δ = 32.6 ppm, an α-methyl ¹H with δ = 1.145 ppm and ³¹P splitting of 0.05 ppm. The second hydrolysis product

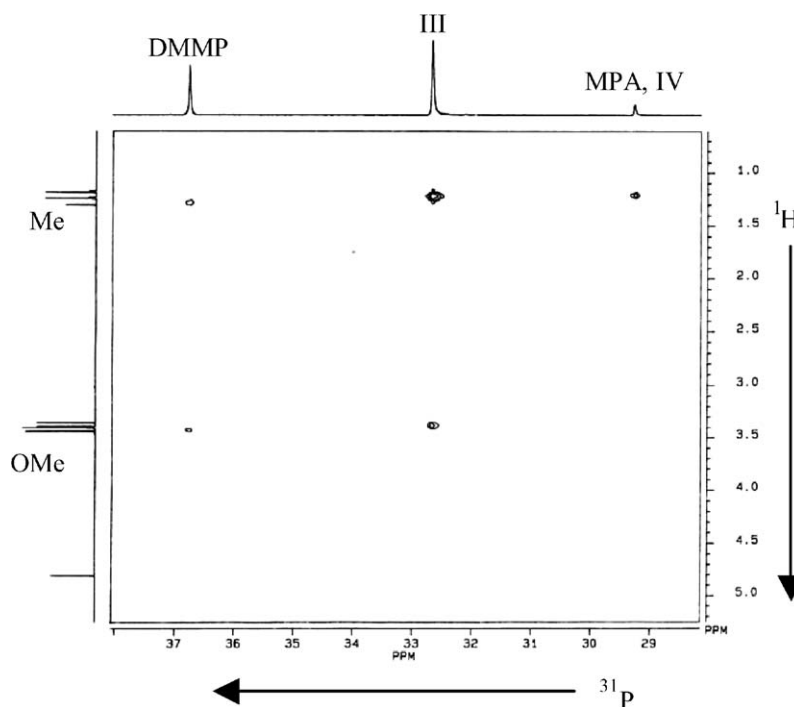


Fig. 1. 2D ³¹P–¹H solution NMR spectrum of the acid hydrolysis equilibrium of DMMP in D₂O.

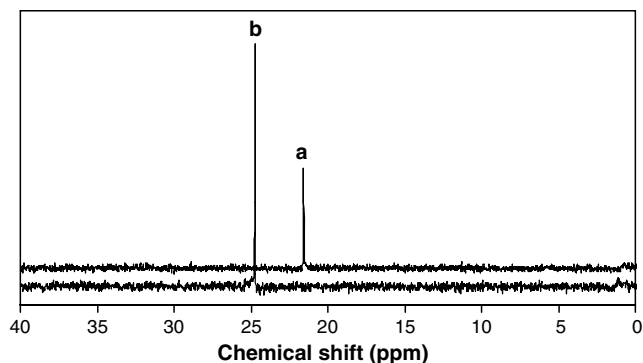


Fig. 2. Solution ^{31}P NMR spectra of the titration of MPA in H_2O to the (a) first and (b) second titration points with NaOH.

MPA (methyl phosphonic acid) has a ^{31}P intensity of about one-tenth that of DMMP and, in agreement with an authentic sample, has a ^{31}P $\delta = 29.2$ ppm and an α -methyl ^1H with $\delta = 1.130$ ppm and ^{31}P splitting of 0.04 ppm. Similar results with significantly different solvent shifts were obtained in THF solvent. See Section 3 for the chemical structures.

2.2. Titration of MPA

MPA (0.1 g in 2 mL H_2O) was titrated to the first and second stoichiometric equivalence points with 0.1 M NaOH in H_2O and the resulting solutions were saved for subsequent solution NMR analysis.

In Fig. 2 are shown the solution ^{31}P NMR spectra of MPA in H_2O solvent, titrated to its first and second NaOH equivalence points. The species at the first equivalence point is the singly charged anion with a chemical shift of 21.6 ppm. The species at the second equivalence point is the doubly charged anion with a chemical shift of 24.8 ppm. See Section 3 for the chemical structures.

3. Experimental results

The solution ^{31}P NMR spectra of the DMMP that remains in the CDCl_3 solvent was examined. The results showed that 99.4% of the DMMP was adsorbed in NaX with no H_2O loaded and >99.99% in NaX with 1–30 molecules of H_2O loaded per unit cell. No DMMP was detected by solution ^1H NMR in the THF washings. Fig. 3 shows the solid state MAS ^{31}P NMR spectra of the NaX and its contents, after DMMP adsorption and subsequent washing at several levels of H_2O loading. For comparison the spectrum of the dry, evaporatively loaded NaX sample is also shown.

The reference titration experiments showed phosphonate $^{1-}$ ion at a solution ^{31}P NMR chemical shift of $\delta = 21.6$ ppm, a singly ionic species, similar to the species (I) which would be found from nucleophilic substitution into DMMP in the absence of water (Structure 2). The reference titration experiments also showed the methylphospho-

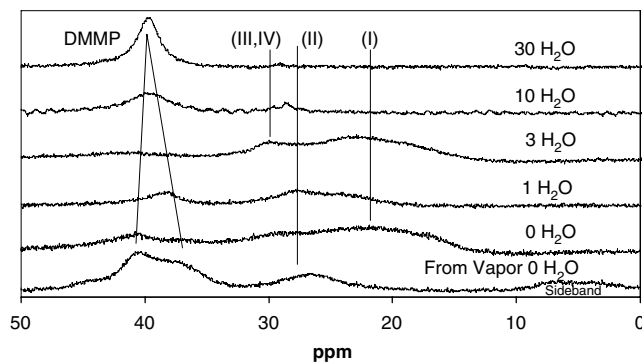
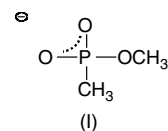


Fig. 3. Solid state MAS ^{31}P NMR spectra of NaX, previously loaded with 0, 1, 3, 10, and 30 molecules per supercage of H_2O , into which DMMP has been loaded at one molecule per supercage via slurry in CDCl_3 solvent and washed with THF. For comparison is also shown the solid state MAS ^{31}P NMR spectrum of dry NaX evaporatively loaded with DMMP at 1 molecule per supercage. Assignments are shown. See Section 3 for the chemical structures of (I–IV).

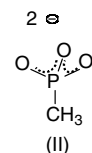


Structure 2.

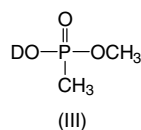
nate $^{2-}$ ion (II) solution ^{31}P resonance at $\delta = 24.8$ ppm in H_2O (Structure 3). Details of the titration experiments are given in the supporting information. The solution ^{31}P NMR analysis of the hydrolysis in D_2O solvent showed that DMMP has $\delta = 36.8$ ppm, its first hydrolysis product (III) has $\delta = 32.6$ ppm, and its second hydrolysis product (IV), MPA, has $\delta = 29.2$ ppm, in agreement with an authentic sample (Structures 4 and 5).

On the basis of the solution NMR studies of DMMP hydrolysis and MPA titration and of the dependence of the results on water loading of the NaX, it is reasonable to assign the solid state MAS ^{31}P chemical shifts in Fig. 3 as follows. The peaks at $\delta = 22.0$ – 22.9 ppm are from (I), assuming that this species has a similar chemical shift to the singly ionic species at the first titration equivalence point. The peaks at $\delta = 26.6$ – 27.6 ppm are from (II). The peaks at $\delta = 28.6$ – 30.00 ppm are from the first or second hydrolysis products, (III) and (IV, MPA).

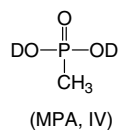
Solid state CP MAS ^{13}C spectra of the NaX and its contents after DMMP adsorption and subsequent washing at several levels of H_2O loading were also examined for the purpose of observing the framework methyl proposed in



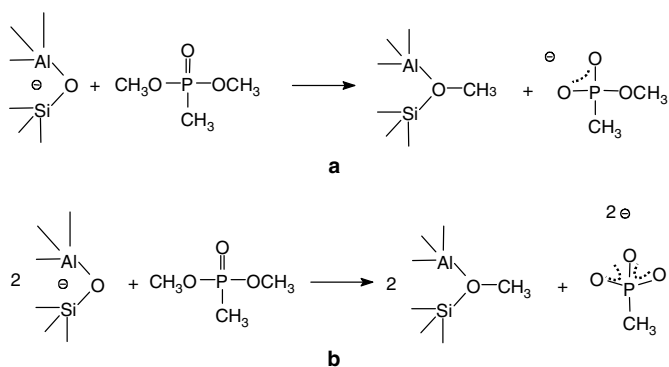
Structure 3.



Structure 4.



Structure 5.



Scheme 1. Proposed mechanism for the formation of ionic products from zeolite nucleophilic substitution into DMMP.

Scheme 1a and b in the following section. A reference solid state MAS ^{13}C NMR spectrum for this species [8–10] was obtained from NaX and its nucleophilic substitution into $^{13}\text{CH}_3\text{I}$, which exhibits a broad peak at about $\delta = 56$ ppm, and is presented in the [supporting information](#).

We have repeated the work of Wagner and Bartram on NaY¹ under our own experimental conditions and have found by solution ^1H NMR that less than 10% of the DMMP is adsorbed into NaY loaded with 0 and 3 H₂O per supercage from CDCl₃ solution. Of the DMMP retained in NaY no detectable amount has been degraded and the remaining DMMP exhibits high mobility, as indicated by an isotropic DMMP solid state MAS ^{31}P NMR peak at a chemical shift of 38.1 ppm. The solid state MAS ^{31}P NMR spectra are shown in the [supporting information](#).

4. Discussion

These results show that in NaX, loaded with amounts of water ranging from 0 to 30 H₂O per supercage, there is substantial DMMP decomposition. Very low levels of DMMP and other P-containing species are found in the CDCl₃ solvent and THF washings. DMMP decomposition is extensive at low levels of added H₂O and DMMP yields exclusively the ionic species (I) and (II). As the amount of water is increased, the relative amount of DMMP

hydrolysis products increases and the total extent of DMMP decomposition of both kinds drops off. Above about 10 H₂O per supercage, the DMMP solid state MAS ^{31}P NMR resonance narrows, indicating substantial hopping from site to site. The constancy of the DMMP solid state MAS ^{31}P chemical shift into the high H₂O range indicates, however, that it has not been displaced to another type of site.

The evidence is consistent with the mechanisms in Scheme 1a and b. In the presence of water, (I) and (II) are hydrolyzed, in agreement with a drop-off in the observation of the ionic species in favor of the hydrolysis products. The framework alkyl proposed in Scheme 1 has been reported in zeolite nucleophilic attack on organohalogens [8–10]. The decreasing tendency for DMMP decomposition in the presence of H₂O may be explained by the electron-withdrawing character of the H₂O via H-bonding to the framework oxygen atoms. This lessens the electron-donating nucleophilicity of the framework oxygens. H₂O coordination to the supercage Na⁺ may also serve to lessen its ability to stabilize the leaving group anions (I) and (II). In other studies [6,11,12] it has been shown that methyl group H atoms have substantial attractive interactions with framework oxygen atoms. The decrease of electron-donating ability of the framework oxygens with increased water content may serve to weaken these methyl group-framework oxygen forces. This effect, together with coordinative H₂O shielding of the Na⁺ electrostatic interactions with DMMP, may be leading to the observed increase in DMMP mobility with H₂O content.

The framework methyl species proposed in Scheme 1a and b may be observable in the solid state CP MAS ^{13}C NMR spectra of the NaX and its contents, after DMMP adsorption and subsequent washing at several levels of H₂O loading. The experimental results exhibited both broad and narrow solid state CP MAS ^{13}C NMR peaks at about $\delta = 54$ ppm. The broad peak is consistent with an authentic sample of the framework methyl species [8–10], which has a broad solid state MAS ^{13}C NMR line at $\delta = 56$ ppm. See [supporting information](#). The broad line is superimposed with the spectrum of residual DMMP, which has a sharp solid state CP MAS ^{13}C NMR peak at $\delta = 54$ ppm, observed in NaX loaded with 30 H₂O. Solid state CP MAS ^{13}C NMR peaks from some residual THF at <1 molecule per supercage levels from the washing process were sometimes also observed, along with a poorly resolved doublet, centered at about $\delta = 10$ ppm. See [supporting information](#). This chemical shift is where the methylphosphonate methyl group of any of the species I–IV would be expected and is where it was observed for DMMP in NaX loaded with 30 H₂O. See [supporting information](#) for details. Both residual DMMP and the framework methyl species in combination with DMMP decomposition products would have a cumulative ~2:1 intensity ratio of framework methyl (or methoxy) to methylphosphonate methyl solid state CP MAS ^{13}C NMR and this was observed for the methyl doublet at about $\delta = 10$ ppm,

shown in the supporting information. Thus these experiments indicate the possible presence of the proposed framework methyl species, sometimes along with residual DMMP depending on experimental conditions, as was seen in the solid state MAS ^{31}P NMR experiments shown in Fig. 3.

The reason for incomplete destruction of DMMP at low H_2O content is not clear. The reaction from the vapor phase and the slightly poorer, 99.4% adsorption of DMMP from the CDCl_3 solvent suggests that a degree of blockage of the zeolite pores, due to already tightly bound, immobile DMMP or its products, may be a factor at low H_2O content. It is clear from the results above that DMMP mobility is enhanced by the presence of H_2O . This may be due to the weakening of the DMMP– Na^+ interaction due to the first few molecules of H_2O that are known to coordinate to the supercage site III or III' Na^+ cations [13]. Other chemical and spectroscopic properties have been shown to depend on the amount of H_2O “spectator molecule” present in the zeolite [14,15]. Moreover, the “spectator” effects were found to be more significant in X zeolites than Y zeolites and dependent on the specific cation [14,15]. It should be emphasized that, although the authors of these studies refer to water as a spectator molecule, the water in the present study participates in hydrolysis of the phosphonate ions. Thus, strictly speaking, water is not a spectator molecule in the present study, although the behavior of the water in the published studies is relevant. It is clear that the zeolite binds DMMP very tightly, even when reaction is incomplete. It would appear that optimal DMMP adsorption and decomposition takes place with 1–3 H_2O per supercage. Room temperature binding of DMMP is relatively fast and is probably diffusion controlled. Experiments with solution NMR of a typical CCl_4 solution of DMMP, containing a typical NaX slurry, indicate that the binding in solution takes place with a $1/e$ time of 4.3 min. IR monitoring of DMMP at its vapor pressure, introduced over NaX powder in a 10 cm IR gas cell, disappears with a $1/e$ time of 2 min. Elevation of the temperature to 100 °C can decompose DMMP completely at this optimum level of adsorption and is thus capable of moving unreacted DMMP to sites, where it can undergo nucleophilic substitution.

We believe that the more encouraging DMMP reactivity of dry NaX in this study than in dry NaY is due to the lower Si–Al ratio of NaX, which enhances the zeolite’s nucleophilicity, and is due to the presence of supercage Na^+ ions, which, in turn, assists the departure of the negatively charged leaving-group after nucleophilic substitution. A similar, lower nucleophilic reactivity of NaY has been observed in our work on nucleophilic substitution into alkyl halides [7]. We also showed that the removal of most of the water from the zeolite enhances reactivity significantly.

In summary, the three objectives of the study have been achieved. There is a high degree of strong adsorption of DMMP in NaX. Significant decomposition of DMMP takes place in NaX in the presence of small amounts of zeo-

litic water. The mechanisms of decomposition of DMMP are by zeolite framework nucleophilic displacement of phosphonate ions and subsequent hydrolysis.

In order to apply the findings of this work to actual conditions in which nerve agents might be remediated and neutralized, further work should be done on the kinetics of adsorption and zeolitic decomposition of DMMP, under conditions simulating fields of application. For similar reasons, the dependence on DMMP loading in the zeolite should be further investigated.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article (experimental details and supporting spectroscopic data) can be found, in the online version, at [doi:10.1016/j.micro-meso.2005.12.018](https://doi.org/10.1016/j.micro-meso.2005.12.018). Information may be found on zeolite drying, stoichiometric water addition, and DMMP adsorption into NaX and NaY. Solid state CP MAS ^{13}C NMR experimental results on NaX loaded with DMMP by various means and an authentic framework methoxy solid state MAS ^{13}C NMR spectrum are shown. Solid state ^{31}P MAS NMR spectra of NaY loaded with DMMP are shown at two levels of water loading.

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