^{31}P MAS NMR study of the hydrolysis of O,S-diethyl phenylphosphonothioate on reactive sorbents

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Abstract

^{31}P MAS NMR was used to monitor the hydrolysis of O,S-diethyl phenylphosphonothioate (DEPPT) sorbed on gamma-alumina, XE-555 (a mixture of strong-acid/strong-base ion exchange resins and a carbonaceous adsorbent), and a polydivinyl-benzene sorbent impregnated with NaOH. The products were identified to determine the amount of P–O/P–S bond hydrolysis occurring on the sorbents. The relative order of reactivity observed for the sorbents is: polydivinylbenzene/NaOH > gamma-alumina ≫ XE-555. Distinct ^{31}P MAS NMR peaks were observed for DEPPT sorbed on the individual components of XE-555. ^{31}P MAS NMR also suggested the presence of mobile and translationally-restricted phases for DEPPT sorbed on gamma-alumina. These aspects of DEPPT sorption provided by ^{31}P MAS NMR enabled a better understanding of the DEPPT reactivity observed on XE-555 and gamma-alumina.

1. Introduction

The U.S. Army is examining the efficacy of self-decontaminating adsorbents (SDAs) as potential replacements for a minimally-reactive adsorbent called XE-555 (trade name of the Rohm and Haas Co.) and the very effective, but highly-corrosive decontaminating solution DS2 [1]. Although XE-555 was originally developed as a non-corrosive skin decontaminant [1], both XE-

555 and DS2 are used in situations where chemical contaminants must be removed quickly from either personal equipment or selected areas on military vehicles. SDAs which rapidly detoxify adsorbed agents offer several advantages over XE-555 such as a reduction in the contact and vapor hazards associated with the adsorbent after exposure to chemical agents, and the elimination of any need to treat the spent adsorbent with other decontaminating solutions. The advantages of SDAs over DS2 are increased material and environmental compatibility, and possible enhanced stability when exposed to air and moisture.

^{31}P MAS NMR has been previously shown to allow in situ monitoring of the hydrolysis of G-agent simulants[1] on reactive sorbents [2,3],

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[1] G-agents possess the basic chemical structure $(RO)(R')P(O)F$. An example is 'Sarin,' also known as 'GB,' which has the structure: $(i\text{-PrO})(CH_3)P(O)F$. Common simulants include p-nitrophenyl diphenyl phosphate $[(C_6H_5O)_2P(O)(C_6H_4\text{-}NO_2)$, PNDP] and dimethyl methylphosphonate $[(CH_3O)_2(CH_3)P(O)$, DMMP].

including those enhanced by catalytic additives [3]. Unlike G-agents, for which hydrolysis yields relatively non-toxic products, the detoxification of VX $[(C_2H_5O)(CH_3)P(O)SCH_2CH_2N(CH(CH_3)_2)_2]$ by hydrolysis is not as straightforward due to the fact that the P–O cleavage product, $(O^-)(CH_3)P(O)SCH_2CH_2N(CH(CH_3)_2)_2$, is only slightly less toxic than VX [1]. Moreover, this anionic product is extremely resistant to further hydrolysis. The present study examines the hydrolysis of a VX simulant, O,S-diethyl phenylphosphonothioate $[(C_2H_5O)(C_6H_5)P(O)SC_2H_5$, DEPPT], on XE-555, gamma-alumina, and a polymeric divinylbenzene sorbent impregnated with NaOH, polyethyleneimine and polyethyleneglycol. The products are characterized to assess the amount of P–O/P–S hydrolysis occurring for DEPPT on the sorbents. In addition to the ability of ^{31}P MAS NMR to monitor the hydrolysis of DEPPT on sorbents, the potential exists for studying the adsorption and distribution of the simulant on mixed sorbent systems due to the extreme sensitivity of the DEPPT ^{31}P chemical shift to its environment. Knowledge of the distribution of adsorbed challenges on mixed sorptive/reactive materials, such as XE-555, is essential to understanding the apparent reactivities of these materials [1,2,4].

2. Experimental

2.1. Materials

DEPPT was synthesized by Dr. Frederic Berg, ERDEC, using the method of DeBruin et al. [5]. The compound was >95% pure (^{31}P NMR). Gamma-alumina (Selexsorb CD, Alcoa) was crushed to a fine powder prior to use. XE-555 (Rohm and Haas Co.), a physical mixture of a high surface area carbonaceous adsorbent and strong-base and strong-acid ion exchange resins, was used as received. Materials similar to those present in XE-555, namely IRA-900 (strong-base ion exchange resin), XN-1010 (strong-acid ion exchange resin), and 348F (high surface area car-

bonaceous adsorbent), were obtained from Rohm and Haas and crushed with a ball mill prior to use. A commercial polymeric divinylbenzene sorbent (Jordi-Gel, Jordi Associates, Inc.) impregnated with reactants [NaOH, polyethyleneimine (PEI) and polyethyleneglycol (PEG)] was provided by Dr. Ralph Spafford, Southern Research Institute. Two samples were prepared by dissolving NaOH, PEI and PEG in methanol which was then added to the sorbent. One sample, JG-PNP-D, was vacuum-dried to remove excess methanol and the other sample, JG-PNP-W, was dried under a stream of nitrogen and contained residual methanol. The two samples were used as received.

2.2. NMR

^{31}P MAS NMR spectra were obtained using a Varian XL200 NMR spectrometer equipped with a Doty Scientific 7 mm high-speed VT-MAS NMR probe as previously described [3]. Samples were typically spun at 3000 Hz. Chemical shifts are referenced to 85% H_3PO_4 with positive shifts lying downfield (higher frequency) from the reference.

In a typical experiment, a measured amount of simulant was syringed into the center of a column of sorbent (ca. 5 mm × 15 mm) contained in a MAS NMR rotor. The volume of sorbent was held constant at 300 μl (the internal volume of the MAS NMR rotor) in every experiment. ^{31}P MAS NMR spectra were acquired over time to monitor the reaction.

2.3. Product identification

Authentic samples of the various hydrolysis and methanolysis products were prepared by reacting DEPPT with 0.2 M NaOH in 50% CH_3CN/H_2O or 50% $MeOH/H_2O$. ^{31}P NMR spectral assignments of the products were made by observing the formation and stability of various species over time. These assignments are given in Table 1.

Although the ^{31}P MAS NMR spectra allowed observation of all products formed on the sorbents, chloroform and/or acidic methanol (80:20

Table 1
^{31}P NMR shift assignments for DEPPT and various reaction products

Compound	Solution	Alumina	XE-555	JG-PNP-W	JG-PNP-D
(EtO)(C$_6$H$_5$)P(O)SEt	48.5 [a], 50.2 [b]	43.5 [c], 44.7 [d]	45.5 [e], 44.7 [f], 44.1 [g], 35 [h]	43.5	43.5
(O$^-$)(C$_6$H$_5$)P(O)SEt	31.4 [a], 32.8 [b]	–	–	27.5	27.9
(MeO)$_2$(C$_6$H$_5$)P(O)	24.3 [b]	–	–	19.0	19.0
(EtO)(MeO)(C$_6$H$_5$)P(O)	22.8 [b]	–	–	19.9	–
(O$^-$)(MeO)(C$_6$H$_5$)P(O)	17.3 [b]	–	–	14.4	14.2
(O$^-$)(EtO)(C$_6$H$_5$)P(O)	15.1 [a], 15.8 [b]	12	13	13.0	13.4

[a] 0.2 M NaOH, 50% CH$_3$CN/H$_2$O.
[b] 0.2 M NaOH, 50% MeOH/H$_2$O.
[c] Immobile, sorbed phase.
[d] Mobile, sorbed phase.
[e] Strong-acid resin component.
[f] Carbonaceous adsorbent component, large pores.
[g] Strong-base resin component.
[h] Carbonaceous adsorbent component, micropores.

MeOH:HCl) were used in attempts to extract neutral and anionic species, respectively, to further characterize the products by solution NMR. For the JG-PNP-W and JG-PNP-D sorbents, the proximity of the ^{31}P NMR resonances of some of the species did not permit unambiguous assignments of the products. The ^{31}P NMR shifts were also found to be quite sensitive to pH and solvent effects which further complicated the assignments. Tentative assignments are indicated where appropriate.

3. Results and discussion

3.1. Gamma-alumina

The left side of Fig. 1 shows the ^{31}P MAS NMR spectra obtained for 20 μl DEPPT added to 0.3285 g gamma-alumina. As shown in 1a, the initial spectrum consists of both a sharp peak at 43.5 ppm and a downfield shoulder at 44.7 ppm. Both peaks are due to DEPPT, although they are slightly shifted upfield from the solution value of 45 ppm (CDCl$_3$). In spectra 1b and 1c, a broad product peak is detected. The ca. 12 ppm chemical shift of the product corresponds to that of the P–S cleavage product ethyl phenylphosphonic acid (EPPA). This product was also detected in extracts of the alumina (see below).

As shown by the reaction profile in Fig. 2, the reaction is rather fast initially. However, the reaction virtually halts after about 10 h. Coinciding with the sudden slowing of the reaction is the disappearance of the downfield shoulder. The experiment was repeated using 5 μl DEPPT which resulted in an identical reaction profile. Likewise, the relative intensities and behavior of the sharp peak and shoulder were also identical in both experiments. These results suggest that the applied DEPPT liquid initially spreads across the alumina surface until, presumably, a 'monolayer' forms. Thus the shoulder at 43.5 ppm is assigned to 'liquid-like' DEPPT, whereas the peak at 42.5 ppm is assigned to 'monolayer' DEPPT. During the initial, rather rapid spreading of the liquid DEPPT, the molecules can react with active sites in a facile manner. However, once the liquid spreading is complete, DEPPT molecules in the 'monolayer' must continue to migrate to active sites in non-wetted areas of the alumina before a reaction can occur. This 'monolayer' diffusion is evidently extremely slow and accounts for the sudden slowing of the reaction after the disappearance of the 'liquid-like' DEPPT.

Addition of 5 drops MeOH/HCl to the sample in the MAS NMR rotor resulted in the reappearance of the shoulder in the ^{31}P MAS NMR spectrum (not shown), although shifted slightly to 47.8 ppm (the main DEPPT peak shifted to 46.0
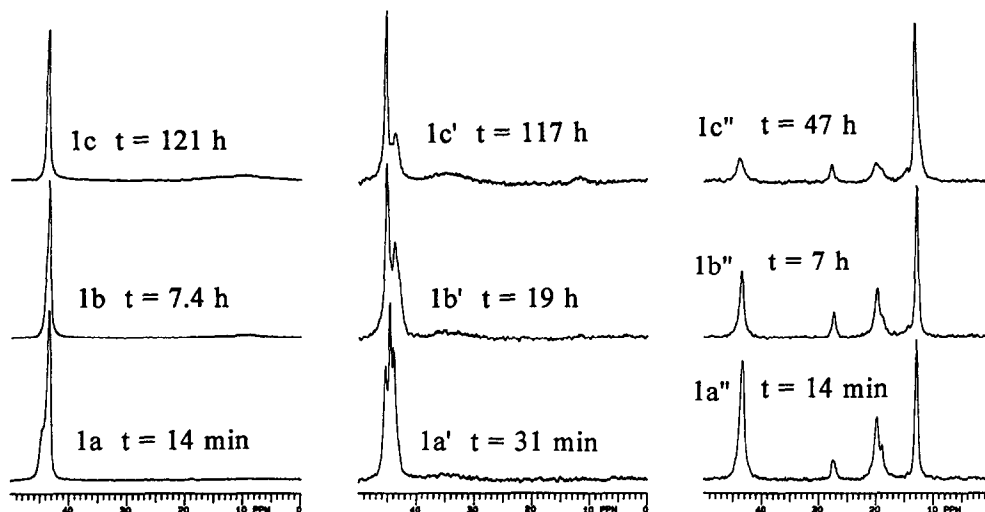
Fig. 1. ³¹P MAS NMR spectra obtained for DEPPT liquid sorbed on gamma-alumina (1a–c), XE-555 (1a'–c') and JG-PNP-W (1a"–1c"). Reaction times are indicated in the Figure.

ppm). Presumably, the solvent dissolved some of the immobile DEPPT to re-form a mobile phase. Also, a sharp product peak was evident at 13.4 ppm along with a broader peak at 15.0 ppm. The peaks are tentatively assigned to the EPPA product and a methanolysis product, ethylmethyl phenylphosphonate (EMPP), respectively. No peak was evident for any P–O cleavage product.

MeOH/HCl extraction of the alumina and analysis by ³¹P NMR revealed DEPPT (49.6 ppm), a species tentatively assigned to EMPP (18.9 ppm) and a small peak at 11.8 ppm assigned to EPPA. No peak was observed for the P–O cleavage product.

3.2. XE-555

The ³¹P MAS NMR spectra in the center of Fig. 1 were obtained for 20 μl DEPPT added to 0.2267 g XE-555. In the initial spectrum (1a'), three sharp overlapping peaks are present at 45.5, 44.7 and 44.1 ppm and a broad peak is evident at 35 ppm, which are due to DEPPT physisorbed on the various components of XE-555 (see below). Over time the peaks at 44.7 and 44.1 ppm decrease while the sharp peak at 45.5 and broad peak at 35 ppm increase (1a'–c'). After about 18 h a product peak at 13 ppm becomes evident (1b'), consistent with the P–S cleavage product EPPA. No other

product peaks are observed. Although sorbed DEPPT undergoes a rather complex redistribution within the XE-555 mixture, hydrolysis is extremely slow as shown in the reaction profile in Fig. 2.

XE-555 is a physical mixture of strong-base/strong-acid ion exchange resins and a high surface area carbonaceous adsorbent. An authentic sample of DEPPT sorbed on IRA-900 (strong-base ion exchange resin) was prepared followed by successive additions of XN-1010 (strong-acid ion exchange resin) and 348F (carbonaceous adsorbent). Changes observed in the ³¹P MAS NMR spectrum after each addition allowed peak assignments to be made for DEPPT adsorbed on the individual materials in the mixture: XN-1010, 47.4 ppm; 348F, 46.9 ppm; and IRA-900, 46.1 ppm. By analogy, the three sharp peaks observed for DEPPT sorbed on XE-555 at 45.5, 44.7 and 44.1 ppm are assigned to DEPPT sorbed on the strong-acid ion exchange resin, capillary-condensed DEPPT in the mesopores of the carbonaceous adsorbent [6], and DEPPT sorbed on the strong-base ion exchange resin components, respectively. The broad peak at 35 ppm is due to DEPPT which is strongly adsorbed within the micropores of the carbonaceous adsorbent component [6]. The assignments are in agreement with the pH dependence observed for
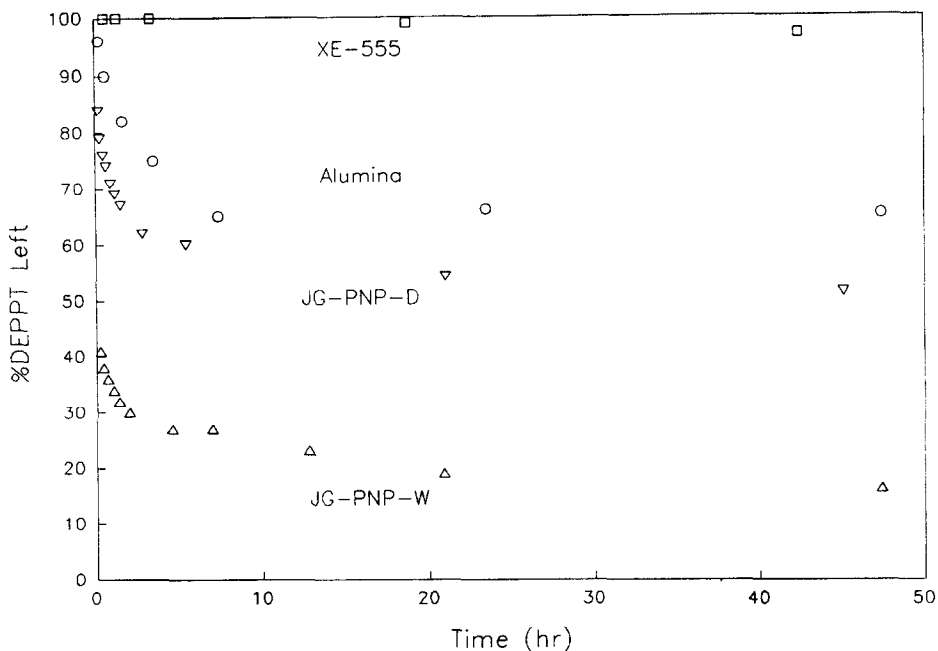
Fig. 2. Reaction profiles for DEPPT sorbed on XE-555, gamma-alumina, JG-PNP-D and JG-PNP-W.

DEPPT in solution and the expected preferential adsorption of DEPPT into the micropores of the carbonaceous adsorbent material. It should be noted that the three sharp, distinct peaks were not observable in previous ^{31}P MAS NMR studies of dimethyl methylphosphonate [$(CH_3O)_2(CH_3)$ $P(O)$, DMMP] sorption on XE-555 [2,4], where a single, sharp peak was detected for DMMP sorbed on the ion exchange resins. However, the broad, upfield-shifted peak was evident for

Scheme 1.

DMMP adsorbed within the carbonaceous component of XE-555 [4].

In the ^{31}P MAS NMR spectrum obtained after adding 5 drops MeOH/HCl to the sample in the NMR rotor, the intensity of the peak assigned to DEPPT sorbed on the strong-acid resin component decreased. Also, two product peaks were evident at 17.7 and 13.2 ppm which, as in the case of gamma-alumina, are similarly assigned to EMPP and EPPA, respectively. No peak was evident for the P–O cleavage product.

An attempt at extracting the products into solution using MeOH/HCl resulted in only the recovery of unreacted DEPPT (50.1 ppm).
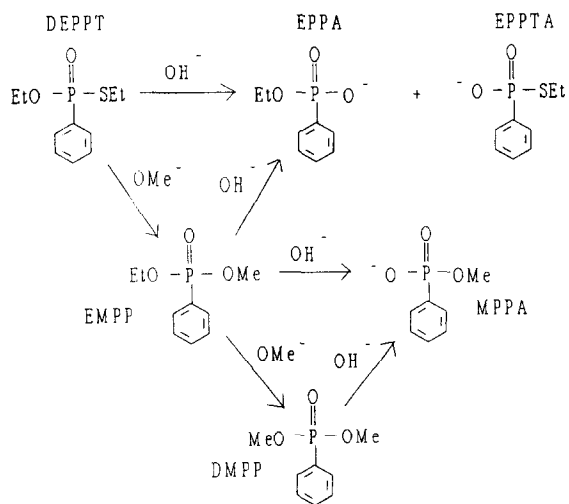
3.3. Polydivinylbenzene/hydroxide

20 μl DEPPT was added to 0.1934 g JG-PNP-D and 0.1975 g JG-PNP-W. These two sorbents differ only in the amount of residual methanol remaining from their preparation. JG-PNP-W contains residual methanol, whereas JG-PNP-D does not. In the ^{31}P MAS NMR spectra of both sorbents, the following peaks (and their assignments) are evident: 43.5 (unreacted DEPPT), 27.5 (S-ethyl phenylphosphonothioic acid,

EPPTA), 19.0 (dimethyl phenylphosphonate, DMPP), 14.4 (methyl phenylphosphonic acid, MPPA), and 13.0 ppm (EPPA). In the spectra obtained for JG-PNP-W (1a″–c″) an additional peak at 19.9 ppm is detected which is assigned to methanolysis product EMPP. In both samples the P–O cleavage product, EPPTA, was persistent but the neutral methanolysis products, EMPP and DMPP, slowly hydrolyzed over time (Scheme 1).

As in the case of gamma-alumina, initial DEPPT hydrolysis rates were relatively fast, but the reaction gradually slowed to an apparent first-order reaction after about 3 h (see reaction profile in Fig. 2). The long-term rate constants are 0.0082 and 0.023 h^{-1} for JG-PNP-D and JG-PNP-W, respectively. Such biexponential behavior has been previously observed for p-nitrophenyl diphenyl phosphate (PNDP) hydrolysis on a strong-base ion exchange resin [3], where the onset of intraparticle diffusion limitations was suggested. The reaction with JG-PNP-W was repeated with 5 μl DEPPT which resulted in a nearly identical reaction profile. Since the amount of NaOH impregnant (7.5 mmol/g) is in large excess of the amount of simulant challenge (0.44 mmol/g for the 20 μl DEPPT experiment), the onset of slow diffusion is the most likely cause of the slow, secondary reaction. The fact that the sorbent containing excess MeOH (JG-PNP-W) provides a markedly faster long-term reaction is also consistent with a diffusion-limited reaction. This latter observation is in agreement with previous work showing the ability of coadsorbed ethanol to increase PNDP hydrolysis rates on both a strong-base resin and XE-555 [2].

The amounts of the P–O cleavage product, EPPTA, represent about 6.8 and 4.8% of the products formed on the JG-PNP-W and JG-PNP-D sorbents, respectively, after the start of the slow, first-order reaction (4.5–5.5 h after addition). The reactions were not followed to completion.

Extraction of the JG-PNP-D sample using chloroform resulted in the presence of unreacted DEPPT (45.7 ppm) and the neutral products, EMPP (20.3 ppm) and DMPP (19.9 ppm). The ^{1}H NMR spectrum obtained for EMPP in the

extract is consistent with data previously reported for this compound [5]. The MeOH/HCl extract contained unreacted DEPPT (50.2 ppm) and two products tentatively assigned to EMPP (21.3 ppm) and EPPA (19.2 ppm).

For the JG-PNP-W sample, MeOH/HCl extraction yielded unreacted DEPPT (50.0 ppm), EPPTA (42.6 ppm), and species tentatively assigned to EMPP (22.6 ppm), DMPP (21.3 ppm), MPPA (20.5 ppm), and EPPA (19.1 ppm).

4. Conclusions

Based on the amount of DEPPT reacting per volume of sorbent, the order of DEPPT reactivity with the sorbents examined is: JG-PNP-W > JG-PNP-D > gamma-alumina ≫ XE-555. Although initially fast, the rate of DEPPT hydrolysis on the JG-PNP sorbents and gamma-alumina slows considerably after about 3 and 10 h, respectively, to enter a first-order regime. Consistent with a diffusion-limited reaction on the polymeric sorbent, residual methanol enhances the reaction rate on the JG-PNP-W sample relative to that observed on methanol-free JG-PNP-D. For XE-555, DEPPT hydrolysis is extremely slow which is attributed to both slow reactions with the strong-acid/strong-base ion exchange resin components and strong adsorption within the micropores of the carbonaceous adsorbent constituent of this material.

The ^{31}P NMR chemical shift of DEPPT is very sensitive to its environment. This feature of the simulant allows distinct peaks to be observed for DEPPT sorbed on the strong-acid ion exchange resin, strong-base ion exchange resin and carbonaceous adsorbent components of XE-555. Furthermore, two signals are observable for DEPPT sorbed on gamma-alumina which are apparently due to mobile and translationally-restricted phases.

For gamma-alumina and XE-555 only the P–S cleavage product, ethyl phenylphosphonic acid (EPPA), is observed. However, the reactions

were not followed to completion and the formation of a small amount of the P–O cleavage product, *S*-ethyl phenylphosphonothioc acid (EPPTA), would not have been detected. For the JG-PNP sorbents, both EPPA and EPPTA are observed. The latter P–O cleavage product represents about 6.8 and 4.8% of the DEPPT applied to the JG-PNP-W and JG-PNP-D sorbents, respectively.

References

[1] Y.-C. Yang, J.A. Baker and J.R. Ward, Chem. Rev., 23 (1992) 1729–1743.
[2] W.T. Beaudry, G.W. Wagner and J.R. Ward, J. Mol. Catal., 73 (1992) 77–90.
[3] W.T. Beaudry, G.W. Wagner and J.R. Ward, J. Mol. Catal., 93 (1994) 221–231.
[4] W.T. Beaudry, G.W. Wagner and J.R. Ward, J. Mol. Catal., 83 (1993) 183–195.
[5] K.E. DeBruin, C.-I.W. Tang, D.M. Johnson and R.L Wilde, J. Am. Chem. Soc., 111 (1989) 5871–5879.
[6] J. Tabony, Progr. NMR Spectrosc., 14 (1980) 1–26.