

Reactions of the nerve agent simulant diisopropyl fluorophosphate with self-decontaminating adsorbents. A ^{31}P MAS NMR study

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Abstract

The room temperature decompositions of the nerve agent simulant diisopropyl fluorophosphate (DFP) sorbed on γ -alumina, polydivinylbenzene (impregnated with NaOH, polyethylene glycol and polyethylenimine) (DVB/NaOH), and Ambergard[®] XE-555, were studied in situ using ^{31}P MAS NMR. Hydrolysis of the P–F bond of DFP was observed on all three sorbents, which effectively detoxifies nerve agents. On XE-555, the competing process of micropore adsorption of DFP into the carbonaceous component of this sorbent was also observed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sorbents which can decontaminate chemical warfare agents (CWA) [1] are being considered as a non-corrosive alternative to the current U.S. Army decontaminating solution DS2 (70% diethylenetriamine, 28% ethylene glycol monomethyl ether, and 2% NaOH), and as a more reactive replacement for the currently fielded sorbent Ambergard[®] XE-555. XE-555, containing strong-acid and strong-base ion exchange resins and a carbonaceous resin, is a non-irritating skin decontaminant that is also employed for decontaminating personal equipment. XE-

555 and DS2 are formulated for use in battle-field situations where rapid decontamination is essential.

Two self-decontaminating sorbent (SDA) candidates, γ -alumina and polydivinylbenzene impregnated with NaOH, polyethylene glycol and polyethylenimine (DVB/NaOH), have shown promising reactivity towards 2-chloroethyl phenyl sulfide (CEPS) [2] and *O,S*-diethyl phenylphosphonothioate (DEPPT) [3]. These compounds are CWA simulants for mustard¹ and VX,² respectively. Previous MAS NMR

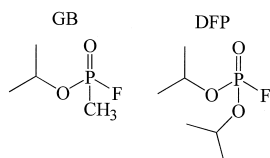
¹ Mustard (or HD), a blister agent, has the structure: $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$.

² VX, a nerve agent, has the structure: $(\text{CH}_3\text{CH}_2\text{O})(\text{CH}_3)\text{-P}(\text{O})\text{SCH}_2\text{CH}_2\text{N}(\text{CH}(\text{CH}_3)_2)_2$.

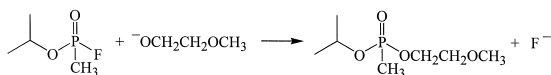
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studies have demonstrated the usefulness of the technique to determine both the reaction chemistry occurring on sorbents, as well as characterizing various adsorption processes. For example, both DEPPT and CEPS were spectroscopically observed to slowly adsorb within the micropores of the carbonaceous component of XE-555 [2–4]. Also, for DEPPT on γ -alumina distinct peaks were observable for both a mobile ‘liquid’ phase and a rather immobile ‘monolayer’ phase, with the disappearance of the mobile phase coinciding with a dramatic slowing of the reaction rate. In the current study, the sorption and reaction of diisopropyl fluorophosphate (DFP) is examined on γ -alumina, DVB/NaOH and XE-555.

DFP is a simulant for a class of nerve agents known as G-agents. Isopropyl methylphosphonofluoridate (Sarin or GB) is perhaps the best widely known example as it was used in the infamous subway attack in Japan in 1995. GB was also implicated in an Iraqi attack on Kurdish communities in Northern Iraq in 1988 [5]. The structures of DFP and GB are shown below.



In DS2, GB is rapidly detoxified via cleavage of the P–F bond by the reactive alkoxide of the ethylene glycol monomethyl ether as shown in Scheme 1 [1]. The P–F bond of DFP is anticipated to be similarly cleaved by the three sorbents, based on the reaction behavior of DEPPT [3].



Scheme 1.

2. Experimental

2.1. Materials

Diisopropyl fluorophosphate (DFP) was purchased from Aldrich. Caution: DFP is highly toxic! XE-555 was obtained from Rohm and Haas. Two γ -aluminas, F-200 and Selexsorb CD, were obtained from Alcoa in the form of 7×14 mesh beads. The beads were crushed to a fine powder prior to use. These sorbents were otherwise used as received. Polydivinylbenzene (DVB) and polyethylene glycol 1450 (PEG) were obtained from Southern Research Institute. Polyethylenimine (MW 700) was obtained from Aldrich.

2.2. DVB/NaOH preparation

Two samples, DVB/NaOH(H_2O) and DVB/NaOH(MeOH), were prepared using water and methanol, respectively, as the impregnation solvent. The preparation is as follows: 2.16 g NaOH was added to 18 ml solvent in a 100 ml Schlenk flask. The solution was stirred using a magnetic stirrer. When the NaOH was dissolved, PEI (2.16 g) and PEG (2.16 g) were then added to the flask. When the solution appeared homogeneous, DVB (4.0 g) was added to the stirred flask. Stirring was continued until all the DVB was thoroughly wetted by the impregnating solution. The solvent was then vacuum-distilled from the flask to yield the DVB/NaOH sorbent. The DVB/NaOH(H_2O) and DVB/NaOH(MeOH) sorbents were stored under nitrogen in the Schlenk flasks.

2.3. NMR

^{31}P MAS NMR spectra were obtained at 81 MHz using a Varian INOVA 200 NMR spectrometer equipped with a Doty Scientific 7 mm High Speed VT-MAS NMR probe. Samples were packed in 7 mm zirconia rotors with KEL-F

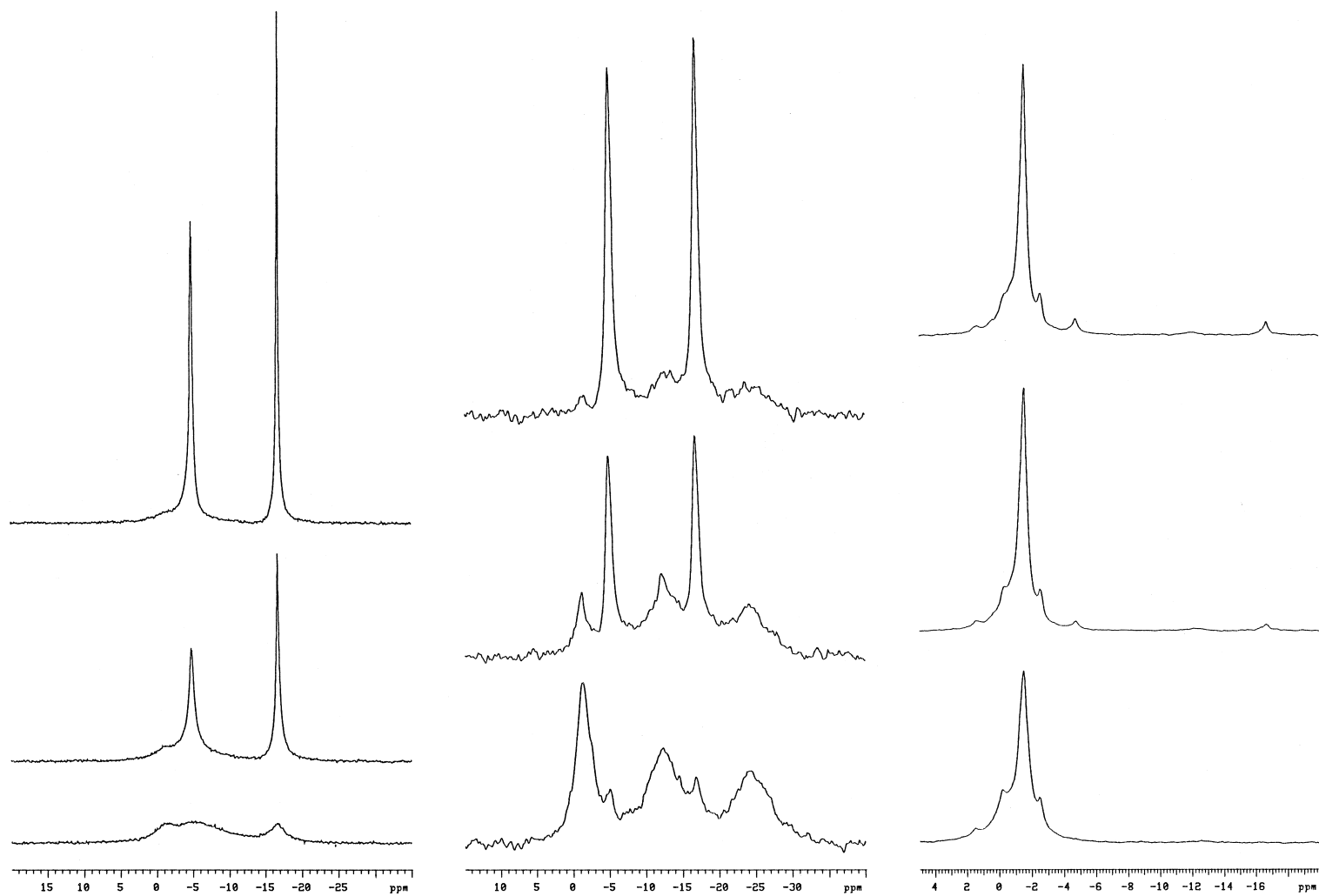


Fig. 1. ^{31}P MAS NMR spectra for DFP on sorbents. Left column: 15 μl DFP on 0.2944 g F-200 alumina at (top to bottom) 15.6 min, 2.19 h and 24.2 h. Middle column: 15 μl DFP on 0.1948 g XE-555 at 11.6 min, 2.12 h and 24.3 h. Right column: 11 μl DFP on 0.2134 g DVB/NaOH(MeOH) at 10.6 min, 21.8 min and 2.0 h.

endcaps. Teflon tape was used to seal the rotors [6]. Spectra were acquired at spinning speeds of 3000–4000 Hz, using 90° observe pulses, 128 scans, 5 s delay between scans, and high power proton decoupling (ca. 50 kHz). Spectra were referenced to external 85% H₃PO₄ (0 ppm).

2.4. Kinetic runs

All reactions were carried out at 23°C. The amount of DFP used was 5–10 wt.% of the sorbent. To initiate the reaction, a measured amount of liquid DFP was syringed into the center of a column of sorbent (5 mm × 15 mm) packed in the 7 mm NMR rotor. The sample was quickly sealed and placed in the spectrometer. ³¹P MAS NMR spectra were acquired periodically to monitor the reaction progress. For each spectrum, the reaction time was taken to be the midpoint of the data acquisition period (11 min). Reactivity results are reported as the percentage of unreacted DFP as calculated using the NMR peak areas measured for the remaining DFP and any products formed.

3. Results

3.1. γ -Alumina

Selected ³¹P MAS spectra obtained for DFP on the F-200 alumina are shown in the left column of Fig. 1. Similar spectra were obtained for the CD alumina. Unreacted DFP is detected as a sharp doublet (–10.8 ppm, $J_{\text{PF}} = 967$ Hz). Over time the DFP peaks become quite broad, but remain unshifted. A distinct peak does not emerge for surface-bound DFP as previously observed for DEPPT [3]; rather peak broadening is the only evidence for the liquid DFP being slowly adsorbed on the surface. The broad peak at ca. –1.3 ppm, which is only a singlet due to cleavage of the P–F bond, is assigned to diisopropyl phosphate (DIP). The reactivity results for the F-200 and CD aluminas are shown in Table 1.

Table 1
DFP reactivity of sorbents^a

Sorbent	10 min	2 h	24 h
DVB/NaOH(MeOH)	6	ND ^b	ND
DVB/NaOH(H ₂ O)	20	4	ND
F-200 alumina	88	60	19
CD alumina	92	63	25
XE-555	98(75) ^c	91(47)	71(9)

^a%DFP remaining.

^bNot detected; estimated detection limit 3%.

^cValues in parentheses reflect the amount of unreacted DFP detected outside the micropores of the carbonaceous component of XE-555.

3.2. XE-555

³¹P MAS NMR spectra of DFP on XE-555 are shown in the middle of Fig. 1. The sharp doublet (–10.8 ppm, $J_{\text{PF}} = 962$ Hz) is due to unreacted DFP outside the micropores [4] of the carbonaceous component of XE-555. The broad doublet (–18.6 ppm, $J_{\text{PF}} = 966$ Hz) is due to unreacted, micropore-adsorbed DFP. The broad singlet at –1.0 ppm is assigned to DIP on the ion exchange resin components [3]. The two sharp features noticeable in the middle spectrum (which sit atop the –1.0 ppm DIP singlet and the –12.5 ppm peak of the broad DFP doublet) may be due to transient isopropyl fluorophosphate (IFP, –6.7 ppm, $J_{\text{PF}} = 921$ Hz) (see below), but this is only a tentative assignment. Over time, the sharp DFP doublet decreases, whereas the DIP singlet and broad DFP doublet increase, demonstrating the competing processes of reaction with the ion exchange resin components and micropore-adsorption within the carbonaceous component. The reactivity data shown in Table 1 is reported in two manners: (1) the percentage of total unreacted DFP, and (2) the percentage of unreacted DFP not adsorbed in the micropores of the carbonaceous component (in parentheses).

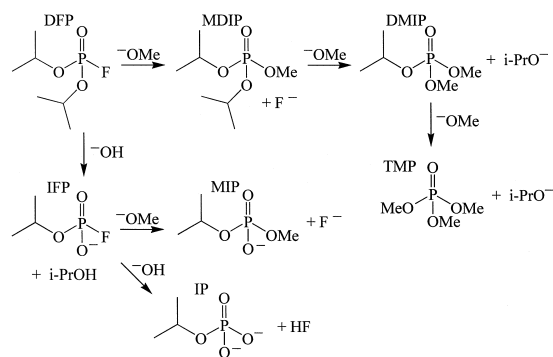
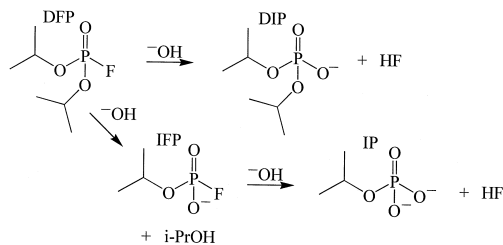
3.3. DVB/NaOH

³¹P MAS NMR spectra of DFP on DVB/NaOH(MeOH) are shown in the right column of

Fig. 1. Similar spectra were obtained for DVB/NaOH(H₂O), but fewer products were detected (see below). Unreacted DFP is detected as a sharp doublet (−10.8 ppm, $J_{\text{PF}} = 966$ Hz). A partially obscured doublet (−6.3 ppm, $J_{\text{PF}} \approx 930$ Hz) is also evident. This species is attributable to either isopropyl fluorophosphate (IFP) or methyl isopropyl fluorophosphate (MIFP), although the broad nature of the peaks suggests that it is IFP as anions tend to possess broadened peaks relative to neutral species. For DVB/NaOH(H₂O), the doublet species is most certainly IFP. Numerous singlet product peaks near 0 ppm, which lack a P–F bond, are attributable to DIP, isopropyl phosphate (IP) and assorted methoxylated phosphates [3]. The major product peak at −1.6 ppm is quite sharp, and is most likely the neutral species methyl diisopropyl phosphate (MDIP). Reactivity data is shown in Table 1.

4. Discussion

All three sorbents possess room temperature reactivity for DFP, resulting in cleavage of the P–F bond. Such a reaction results in the detoxification of GB. On DVB/NaOH(H₂O), XE-555 and the aluminas, hydrolysis occurs to yield DIP. A minor amount of IFP is detected on DVB/NaOH(H₂O), and perhaps also on XE-555, which is further hydrolyzed to IP. A species attributable to IP is clearly detected on DVB/



NaOH(H₂O). These reactions are shown in Scheme 2.

For the DVB/NaOH(MeOH) sorbent, cleavage of the P–F bond occurs much faster than on DVB/NaOH(H₂O). This high reactivity is attributable to the presence of methoxide, and is analogous to the DS2 reaction (Scheme 1). The DFP/methoxide reaction is shown in Scheme 3. The major product, which possesses a sharp ³¹P MAS NMR peak, is consistent with the neutral MDIP species. Other sharp peaks in the ³¹P MAS NMR spectra are consistent with the neutral dimethyl isopropyl phosphate (DMIP) and trimethyl phosphate (TMP) species. The IFP species may undergo either methanolysis or hydrolysis to yield methyl isopropyl phosphate (MIP) or IP, respectively.

5. Conclusions

DVB/NaOH possesses the best reactivity towards DFP, with DVB/NaOH(MeOH) outperforming DVB/NaOH(H₂O) due to the presence of highly reactive methoxide. The reaction of DFP on γ -alumina is much slower, but still faster than on XE-555. On XE-555, the competing processes of reaction with the ion-exchange resin components and micropore adsorption within the carbonaceous component are observed.

References

- [1] Y.-C. Yang, J.A. Baker, J.R. Ward, *Chem. Rev.* 92 (1992) 1729–1743.
- [2] G.W. Wagner, P.W. Bartram, *J. Mol. Catal. A: Chemical* 111 (1996) 175–180.
- [3] G.W. Wagner, P.W. Bartram, *J. Mol. Catal. A: Chemical* 99 (1995) 175–181.
- [4] G.W. Wagner, B.K. MacIver, Y.-C. Yang, *Langmuir* 11 (1995) 1439–1442.
- [5] R.M. Black, R.J. Clark, R.W. Read, M.T.J. Reid, *J. Chromatogr. A* 662 (1994) 301–321.
- [6] W.T. Beaudry, G.W. Wagner, J.R. Ward, *J. Mol. Catal.* 93 (1994) 221–231.