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**SOLID-STATE ^{31}P MAGIC ANGLE SPINNING (MAS) NMR STUDY
OF THE PARTITIONING AND REACTION
OF ORGANOPHOSPHORUS ESTERS ADSORBED
ON SYNTHETIC RESIN CATALYSTS**

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RESEARCH DIRECTORATE

September 1992

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13. ABSTRACT (Maximum 200 words) A powder containing sorptive and reactive resins that was developed for the removal and subsequent catalytic degradation of toxic organophosphorus esters is characterized using dimethyl methylphosphonate (DMMP), p-nitrophenyl diphenyl phosphate (PNDP), and ^{31}P MAS NMR. The results for DMMP confirm, spectroscopically, that adsorbed ester partitions between the sorptive and reactive resin components. Spectra of the DMMP surface probe adsorbed on the resin are indicative of two different adsorption sites, one possessing a much larger capacity compared to the other. The large capacity site is assigned to the reactive resins, and the smaller capacity site is assigned to the sorptive carbonaceous resin. Variable temperature ^{31}P MAS NMR results for DMMP demonstrate that any molecular exchange between these sites must be occurring at a rate less than 300 s^{-1} , even at $50\text{ }^{\circ}\text{C}$. The PNDP hydrolyzes on the resin powder to yield diphenyl phosphate (DPP) and p-nitrophenoxide.				
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PREFACE

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OF THE PARTITIONING AND REACTION
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ON SYNTHETIC RESIN CATALYSTS**

1. INTRODUCTION

Characterizing chemical reactions on synthetic resins is of current interest in our laboratory, since such resins may be tailored to adsorb and react with toxic organophosphorus esters that inhibit cholinesterase activity.¹ In particular, macroreticular resins possess a porous network, which should enhance adsorption and provide sites to attach reactive functional groups.^{2,3} The U.S. Army recently adopted the M291 kit for skin decontamination using macroreticular resins⁴ in lieu of natural clays such as "Fuller's earth." The resin employed is actually a mixture of three components: a high surface area, carbonaceous macroreticular styrene/divinylbenzene resin and two macroreticular styrene/divinylbenzene ion exchange resins. The strong acid resin contains sulfonic acid groups while the strong base resin has quaternary ammonium hydroxide groups. In solution, the toxic, cholinesterase-inhibitors, such as sarin or soman, are rapidly hydrolyzed in strong base and also exhibit acid-catalyzed hydrolysis.⁵

In order for the resin mixture to function catalytically, molecular exchange must exist between the sorptive and reactive sites, and the reactive sites must be able to effect a heterogeneous reaction with the adsorbed liquid. Previous studies in our laboratory with O,O'-diisopropylphosphonofluoridate (DFP) have suggested partitioning in the resin mixture.⁶ Evidence of this partitioning is the apparent low reactivity observed for DFP adsorbed on the resin, despite the apparent high reactivity with the individual reactive resin component. The nature of this partitioning must be understood to design effective systems, which both adsorb and react with liquid contaminant.

This study employs ^{31}P Magic Angle Spinning (MAS) NMR to probe the adsorption and reaction of organophosphorus esters at the molecular level. ^{31}P MAS NMR is perhaps uniquely suited for this purpose, since NMR cannot only distinguish various molecular adsorption sites⁷⁻¹⁰ but can also determine the occurrence and rate of molecular exchange between adsorption sites.¹¹⁻¹⁵

2. EXPERIMENTATION

Ambergard[®] XE-555 Resin, Amberlite[®] IRA-900 Strong Base Resin, Amberlyst[®] XN-1010 Strong Acid Resin and Amborsorb[®] 348F,

563, 564, 572, and 575 Carbonaceous Adsorbents were obtained from Rohm & Haas Company. The IRA-900, XN-1010, and carbonaceous adsorbents, manufactured as small beads, were crushed with a ball mill to yield fine powders. The strong base IRA-900 resin, initially in the chloride form, was exchanged with an aqueous 5% NaOH solution to yield the hydroxide form. The resin was subsequently washed with deionized water to remove NaCl and excess NaOH, filtered, and dried in air at room temperature.

The dimethyl methylphosphonate (DMMP) liquid was loaded onto the resins by stirring weighed amounts of the resin with weighed amounts of DMMP in a small vial. The DMMP vapor was loaded onto the resins by drawing air through a glass pipet containing a small plug of cotton impregnated with a few drops of DMMP. The vapor was allowed to pass through another pipet containing the resin placed in between the DMMP vapor source and the vacuum. Prior to vapor loadings, resins were preequilibrated with room air by drawing air through the pipet containing the resin for a few hours. The difference in weight of the pipet containing the resin after the vapor loading was taken to reflect the amount of DMMP adsorbed and was used to calculate the approximate weight-percent loading. No attempt was made to measure the amount of water lost during the vapor loading process.

The p-nitrophenyl diphenyl phosphate (PNDP) solid was loaded onto the resins by initially dissolving the compound in 95% (v/v) ethanol/water. The solution was then slurried with the resin in a petri dish and allowed to evaporate at room temperature in a fume hood.

Solution ^{31}P NMR spectra were obtained at 81 MHz on a Varian XL-200 NMR spectrometer. ^{31}P MAS NMR spectra were obtained at 101 MHz using high-power proton decoupling on a home-built 6T FT NMR spectrometer equipped with a Doty Scientific, variable temperature, 5mm double-tuned MAS probe. ^{31}P spin-lattice relaxation times (T_1) of less than 2 s are observed for adsorbed DMMP and PNDP that are greatly reduced from their solution values. The short T_1 values alleviate the need for the cross-polarization (CP) technique and favor the more quantitative conventional FT experiment. More importantly, the highly mobile, liquid-like species are not observable using CP due to motional averaging of the ^1H - ^{31}P dipolar interaction. Therefore, the conventional FT experiment was used. All chemical shifts were referenced to an external sample of 85% H_3PO_4 . Positive chemical shifts are at higher frequency (lower field) than the reference.

3. RESULTS FOR DMMP

The first phase of the study involves identifying the various adsorption sites on the resin powder. The DMMP is an

ideal candidate for this purpose since it is a small, simple molecule that is stable except at very high or low pH. Therefore, the molecule is not expected to react rapidly with the acid or base groups on the resin. This surface probe permits NMR spectra, which are not complicated by interfering reaction products and that allow for the straightforward observation of chemically different adsorption sites, to be obtained.

^{31}P NMR spectra of DMMP vapor adsorbed on the resin powder are shown in Figure 1. The top spectrum, 1(a), was obtained under normal solution NMR conditions and reveals two overlapping peaks at 38 and 29 ppm. The relative narrowness of these resonances immediately indicates that DMMP is undergoing fast isotropic "liquid-like" motions on the resin, which averages the broad chemical shift anisotropy (CSA) powder pattern expected for static organophosphorus esters.¹⁶⁻¹⁹ The bottom spectrum, 1(b), was obtained using MAS with high-power proton decoupling. This technique greatly enhances the resolution of the twin peaks as compared to the spectrum obtained without MAS. The narrow downfield resonance occurs at 36.2 ppm, which is the same value observed for DMMP in methanol solution. Methanol extraction of the DMMP from the resin results in only the presence of DMMP in the filtrate; thus, initially, DMMP does not react with the resin but, in fact, resides in two different adsorption sites. The spectra further show that any molecular exchange occurring between the two sites is slow on the NMR timescale ($1-10^{-6}$ s) by virtue of the presence of both individual resonances.²⁰ The width of the peaks in the lower MAS spectrum (ca. 100 Hz) places an upper limit on the exchange rate of 300 s^{-1} at room temperature.

To identify the nature of the two adsorption sites, ^{31}P MAS NMR spectra were obtained for DMMP vapor adsorbed on two ion exchange resins and several carbonaceous adsorbents similar to the reactive and sorptive components in the resin powder. These spectra are shown in Figure 2. The rather broad appearance of the resonance detected for DMMP adsorbed on the 348F carbonaceous adsorbent [2(a)] is characteristic for all the carbonaceous adsorbents and indicates that the molecules are rather rigidly held as further evidenced by the CSA sidebands. However, the actual chemical shifts vary from 31.7 ppm (348F) to 25.6 ppm (572) (see table) and are significantly shifted from the solution value of 36 ppm. Conversely, DMMP remains highly mobile on the strong base and strong acid ion exchange resins [2(b),(c)], yielding sharp resonances at 36.9 and 36.3 ppm, respectively. In the spectrum of the strong base resin, 2(b), a second signal occurs at 25.5 ppm but is due to the slow-forming hydrolysis product methyl methylphosphonate (MMP). Therefore, the two sites detected in XE-555 are assigned to DMMP adsorbed on the ion exchange resins and the carbonaceous adsorbent. A complete listing of ^{31}P MAS NMR assignments for DMMP adsorbed on the various resins is given in the table.

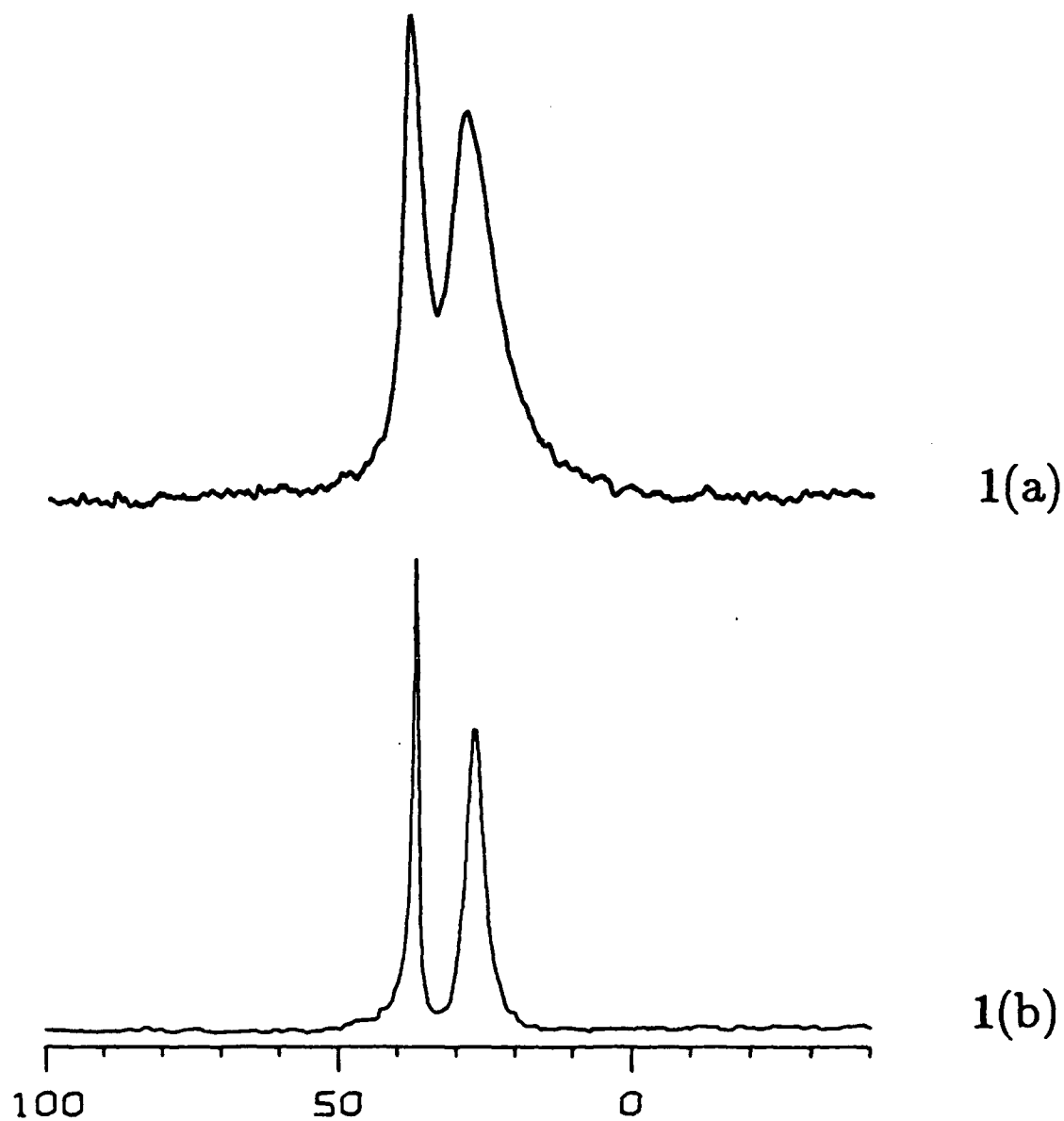


Figure 1. ^{31}P NMR Spectra of DMMP Vapor Loaded on the Resin Powder (<5 wt%) Obtained Using (a) Normal Solution NMR Conditions and (b) MAS and High-Power Proton Decoupling

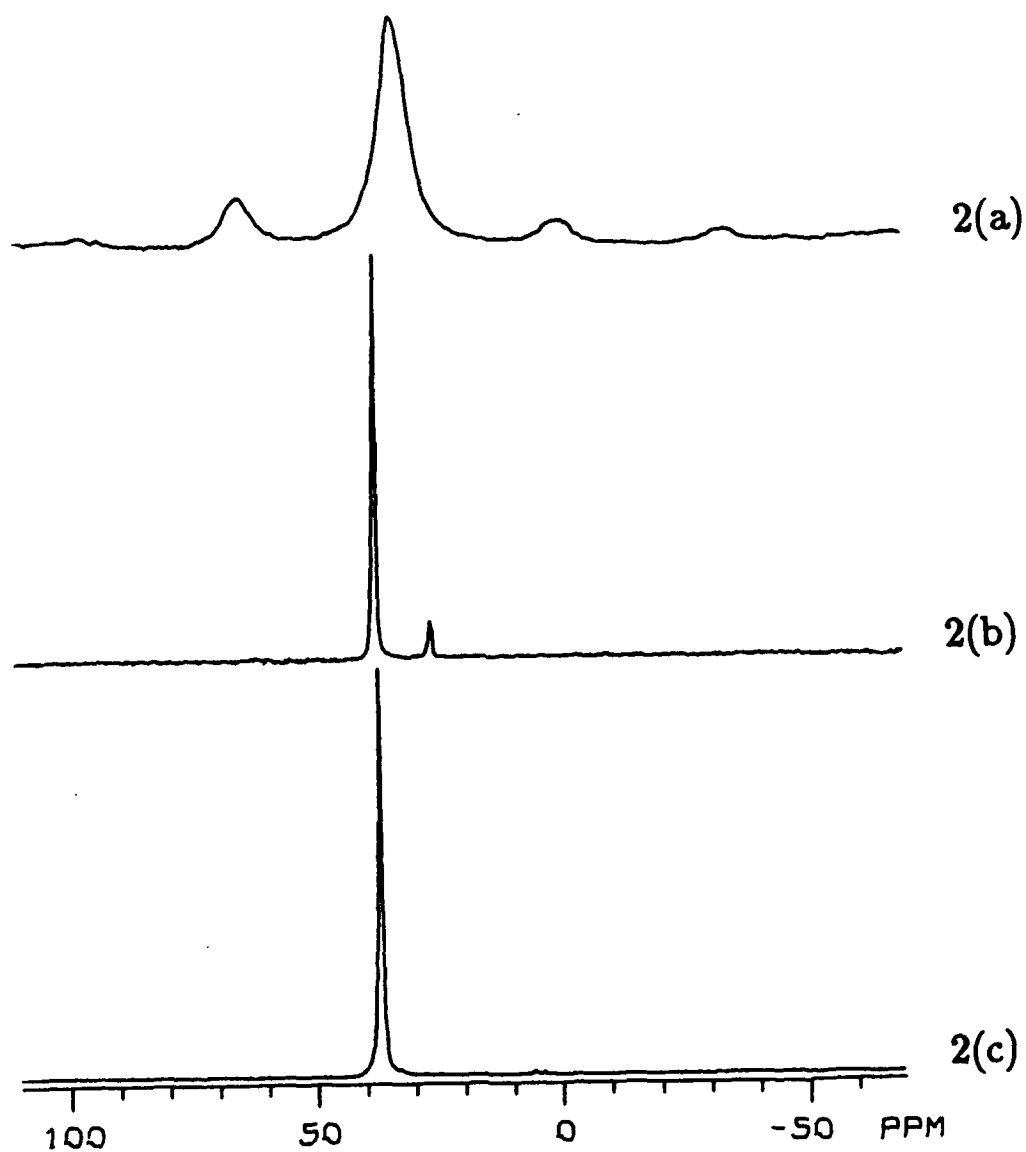


Figure 2. ^{31}P MAS NMR Spectra of DMMP Vapor Loaded on (a) 348F Carbonaceous Adsorbent, 15 wt%; (b) Strong Base Ion Exchange Resin, ca. 3 wt%; and (c) Strong Acid Ion Exchange Resin, 44 wt%

Table. ³¹P MAS NMR Assignments for Organophosphorus Esters Adsorbed on Various Resins

Ester	XE-555	Carbonaceous Adsorbents	IRA-900(OH ⁻)	XN-1010
DMMP	36.2 ^a 26.3 ^b	31.7 (348F) 31.3 (563) 26.0 (564) 25.6 (572) 26.7 (575)	36.9 25.5 ^c	36.3
PNDP	-17.9	-17.8 (348F)	-17.1	-17.9
DPP	-10.1	-	- 9.6	-
DPPA ^d	-	-	-	-10.7
PNPPA ^e	-	-	-	-11.7

^aIon exchange resin components

^bCarbonaceous adsorbent component

^cMethyl methylphosphonate hydrolysis product

^dDiphenyl phosphoric acid

^ep-Nitrophenyl phenyl phosphoric acid

³¹P MAS NMR spectra obtained from samples of various DMMP weight-percent loadings (Figure 3) indicate that adsorption on the carbonaceous adsorbent is favored during small weight-percent vapor loadings. Conversely, the ion exchange resins are allowed to fill at large weight-percent liquid loadings. The small sharp signals in spectrum 3(a) at 24.6 and 6.1 ppm are due to impurities present in the DMMP. The gravimetrically determined weight-percent loadings are only approximate values, since the amount of moisture possibly displaced or lost during the loading process is not known. The relative ratio of the two resonances in all of these spectra did not change over several days, indicating that the DMMP partition achieved during the loading process is stable at room temperature. We note that DMMP does not redistribute to maintain the same constant ratio between the two sites.

A reasonable explanation for the adsorption behavior is that the relatively hydrophobic carbonaceous adsorbent possesses a limited number of fairly strong adsorption sites for DMMP vapor, whereas the hydrophilic ion exchange resins can adsorb gross amounts of DMMP vapor at somewhat weaker sites. The reported water content of the strong base and acid resins are ca. 70 and 50%, respectively; but, the carbonaceous adsorbent contains less than 2% water. In contrast to the ion exchange

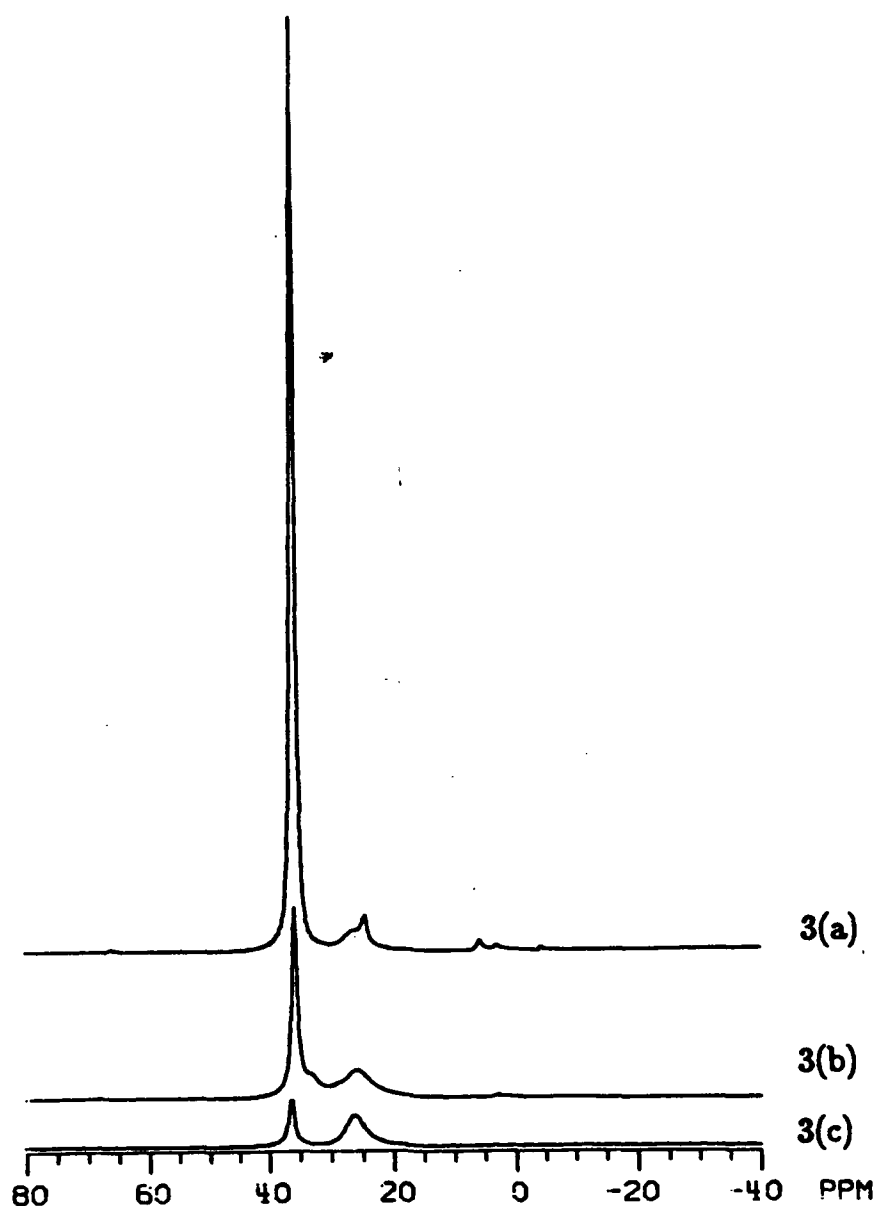


Figure 3. ^{31}P MAS NMR Spectra of DMMP Adsorbed on the Resin Powder Obtained for the Following Weight-Percent Loadings: (a) Liquid Loaded, 148%; (b) Vapor Loaded, 22%; and (c) Vapor Loaded, <5%

resins, DMMP vapor adsorbed on the carbonaceous adsorbent is rather rigidly held. Thus, mobile "liquid-like" DMMP does not seem to be able to form in the pore structure of this resin during the DMMP vapor exposure times examined; whereas, the ion exchange resins are able to rapidly adsorb DMMP vapor to yield liquid-like DMMP in their pores. All three resins rapidly assimilate DMMP liquid to yield adsorbed DMMP, which is highly mobile and liquid like.

The possibility of chemical exchange between the carbonaceous adsorbent and the reactive ion exchange resins was further investigated by variable temperature ^{31}P MAS NMR. For exchanging species, sharp NMR lines are detected when the rate of exchange is either slow or fast on the NMR timescale.²⁰ For slow exchange, sharp distinct signals are detected for each species; however, for fast exchange, a single sharp line is observed at the population-weighted average chemical shift of the two resonances. By varying the temperature of the sample, one can change the rate of molecular motion to effect either the slow or fast exchange regime. The expected sequence of events when changing the temperature from the slow exchange regime to the fast exchange regime is a severe broadening and eventual merging of the two peaks followed by sharpening to the single averaged peak. Variable temperature spectra recorded up to 50 °C for DMMP vapor adsorbed on the resin powder (not shown) yield no features attributable to molecular exchange. On the contrary, at the higher temperatures, the lines actually sharpen due to the increased rate of motion of the molecules within their respective adsorption environments. If molecular exchange was occurring between the sites at a rate approaching the width of the resonances (ca. 100 Hz), then a significant line broadening contribution would be evident as the temperature is raised. Therefore, molecular exchange is very slow (less than 300 s⁻¹) even at 50 °C.

It should be noted that molecular exchange between the sites must occur at an appreciable rate in order for the resin to function as an effective catalyst. The lack of a fast exchange, as seen for DMMP, could account for the slow reaction rate found for DFP in our previous study.⁴

4. RESULTS FOR PNDP

Unlike the DMMP surface probe, PNDP is expected to be more unstable with respect to hydrolysis²¹⁻³¹ and, thereby, to react rapidly with the acid and base groups in the resin powder. In basic solution, the major hydrolysis products are diphenyl phosphate (DPP) and p-nitrophenoxide (a yellow chromophore), although significant amounts of p-nitrophenyl phenyl phosphate (PNPP) and phenoxide also form.^{21,24} For acid-catalysis, diphenyl phosphoric acid and p-nitrophenol are the sole reported products.³¹ The PNDP is a white solid at room temperature, which

necessitates the use of a solvent to load the compound onto the resin.

³¹P MAS NMR spectra of PNDP adsorbed on the resin powder from 95% (v/v) ethanol/water solution are shown in Figure 4. Two peaks are present at -10.1 and -17.9 ppm in the spectrum of a 1-day-old sample, 4(a). The large upfield peak at -17.9 ppm, which has the same chemical shift observed for PNDP in solution,²¹ is assigned to PNDP adsorbed on the ion exchange resins and/or the carbonaceous adsorbent. The spectrum observed for adsorbed PNDP is different than the spectrum of neat PNDP solid,^{*} indicating that the ester does not merely precipitate as the ethanol evaporates but is fairly well dispersed on the resin. The lack of spinning sidebands for the two peaks indicates that both adsorbed PNDP and the other adsorbed species are highly mobile and "liquid like." The small downfield peak at -10.1 ppm is due to the hydrolysis product, DPP, as confirmed by extraction and analysis by solution NMR;²¹ however, no PNPP product is detected. Thus, the observed DPP hydrolysis product demonstrates that the reactive sites are accessible to PNDP, although distinct signals are not observed for PNDP adsorbed on the ion exchange resins and the carbonaceous adsorbent.

Solvents play a major role in polymer-supported solution-phase catalysis,^{2,3} and ordinarily, the resin powder would only contain adsorbed water. Therefore, the effect of coadsorbed ethanol on the reaction was investigated in the following experiment. A PNDP/ethanol loaded sample was allowed to dry in air just to the point where no visible solvent remained, at which time a portion of the sample was removed and placed in a capped 5mm NMR tube. The rest of the sample remained exposed to air to allow further unrestricted loss of ethanol. The portions were allowed to stand for 23 days before their ³¹P MAS NMR spectra were recorded. These spectra are shown in Figures 4(b) and (c). For the capped sample, the conversion of PNDP to DPP is nearly

^{*}The room temperature ³¹P MAS NMR spectrum of neat PNDP solid yields two resonances at -17.9 and -12.6 ppm, which also display completely isotropic CSA's indicative of rapid isotropic molecular tumbling within the crystal lattice of the solid. The relative intensity of the two signals vary smoothly as the temperature is raised with the downfield resonance nearly disappearing just prior to the melting point at ca. 50 °C. As the temperature is lowered, a rather abrupt onset of an observable CSA occurs at ca. -45 °C where the two resonances are of equal intensity. This infers the presence of two equally populated crystal lattice sites in the rigid phase formed at this temperature. Similar behavior has recently been observed for crystalline phosphoric acid although only a single resonance is detected in the low temperature rigid phase of this solid.³²

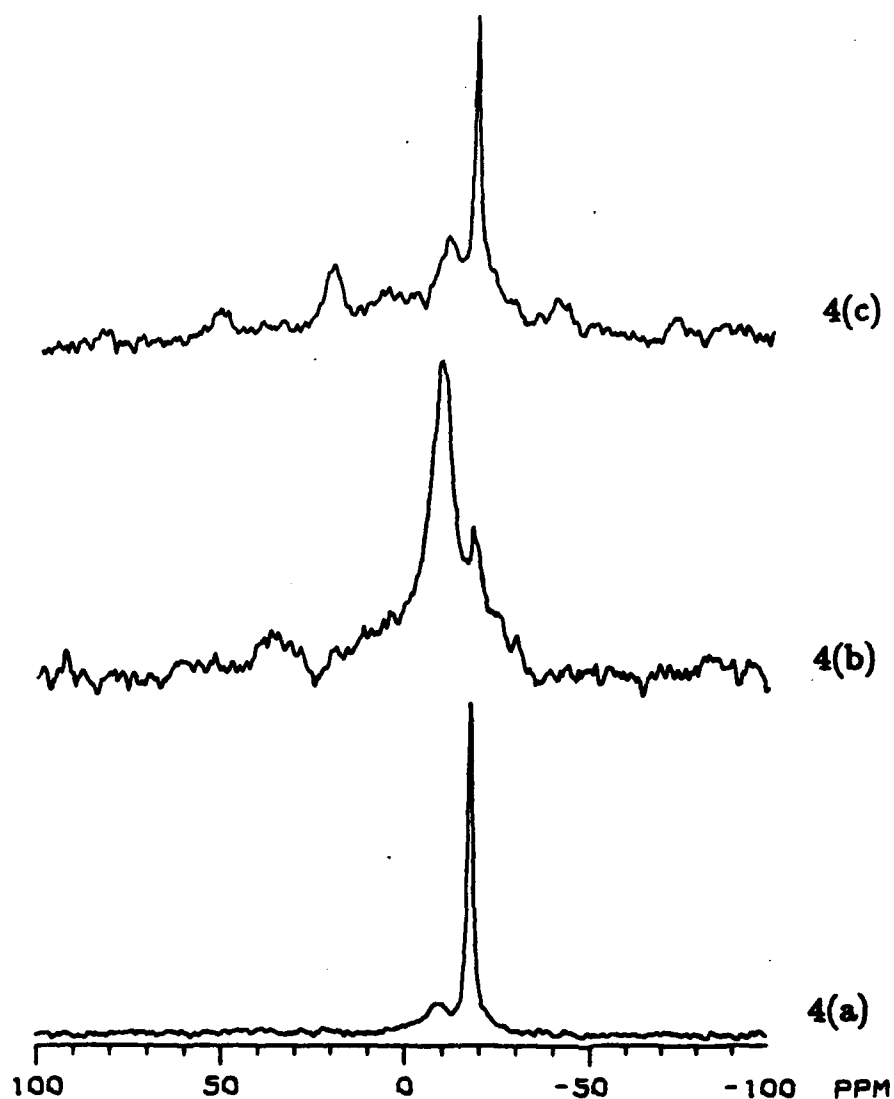


Figure 4. ^{31}P MAS NMR Spectra of PNBP Adsorbed on the Resin Powder from Ethanol Solutions: (a) 1-Day-Old Sample, Stored in a Capped 5mm NMR Tube; (b) 23-Day-Old Sample, Stored in a Capped 5mm NMR Tube; and (c) Same as (b) Except that the Sample Remained Exposed to Air

complete with only a small signal remaining for unreacted PNDP. Also, note that the signal for DPP lacks CSA spinning sidebands, indicating that the product is still very liquid like. However, the spectrum of the air-exposed portion reveals a reduced conversion along with a DPP product that is being very rigidly held by the resin. These observations suggest that coadsorbed ethanol facilitates the hydrolysis reaction, most likely by enabling faster PNDP diffusion to available reactive sites rather than allowing release of DPP product. In fact, acidification is necessary to extract the anionic product into solution. This is a further indication that the DPP anion remains bound to the quaternary ammonium ion exchange sites in the presence of water. Conclusive evidence that ethanol enhances the reaction rate is given by the fact that a PNDP/ethanol solution left in contact with the resin powder in a sealed vial yields a complete conversion of PNDP to DPP in less than 4 days. Therefore, PNDP hydrolysis on the neat resin powder appears to be hindered by slow PNDP migration to the reactive sites in the absence of coadsorbed ethanol.

To determine the reactivity of PNDP with the various components of the resin powder, ^{31}P MAS spectra were also recorded for PNDP adsorbed on a carbonaceous adsorbent and the strong acid and strong base ion exchange resins. These spectra are shown in Figure 5. Spectrum 5(a) of PNDP adsorbed on 348F yields a single peak at -17.8 ppm, which confirms the previous assignment of this resonance to PNDP adsorbed on the carbonaceous adsorbent. As expected, no reaction products are observed on this purely sorptive component. The PNDP adsorbed on the strong base resin hydrolyzes in the same manner as on the resin powder as indicated by the peak at -9.6 ppm in spectrum 5(b), which is similarly assigned to the hydrolysis product DPP. In support of this assignment, the initially tan strong base resin rapidly becomes yellow after being slurried with the PNDP/ethanol solution, consistent with the release of the p-nitrophenoxide chromophore. The strong base resin further parallels the resin powder behavior in that the spectrum of an air-exposed, 15-day-old sample, 5(c), also shows a poor conversion along with a large CSA for the immobilized DPP product; whereas, the capped control sample [Spectrum 5(d)] yields a much better conversion along with a highly mobile, liquid-like DPP product. Again, these findings are consistent with the DPP anion remaining bound to the quaternary ammonium ion exchange sites and slow PNDP migration in the absence of coadsorbed ethanol.

Spectra obtained for PNDP adsorbed on the strong acid resin, Figure 6, are quite different than the spectra obtained for both the resin powder and strong base resin. Again, the peak at -17.9 ppm in the spectrum of the 1-day-old sample, 6(a), is due to adsorbed PNDP. The peaks at -10.7 ppm and -11.7 ppm are assigned to the acid-catalyzed hydrolysis products, DPPA, and

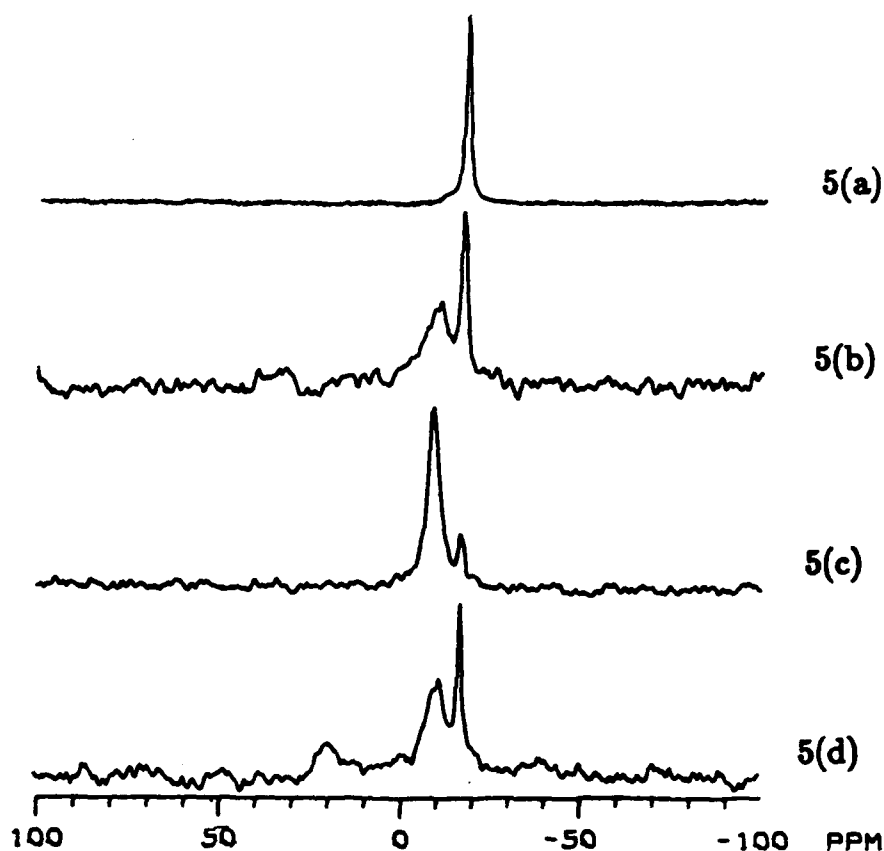


Figure 5. ^{31}P MAS NMR Spectra of PNBP Adsorbed on (a) 348F Carbonaceous Adsorbent, 1 Day Old, Stored in a Capped 5mm NMR Tube; (b) Strong Base Ion Exchange Resin, 1 Day Old, Stored in a Capped 5mm NMR Tube; (c) Strong Base Ion Exchange Resin, 15 Days Old, Stored in a Capped 5mm NMR Tube; and (d) Same as (c) Except that the Sample Remained Exposed to Air

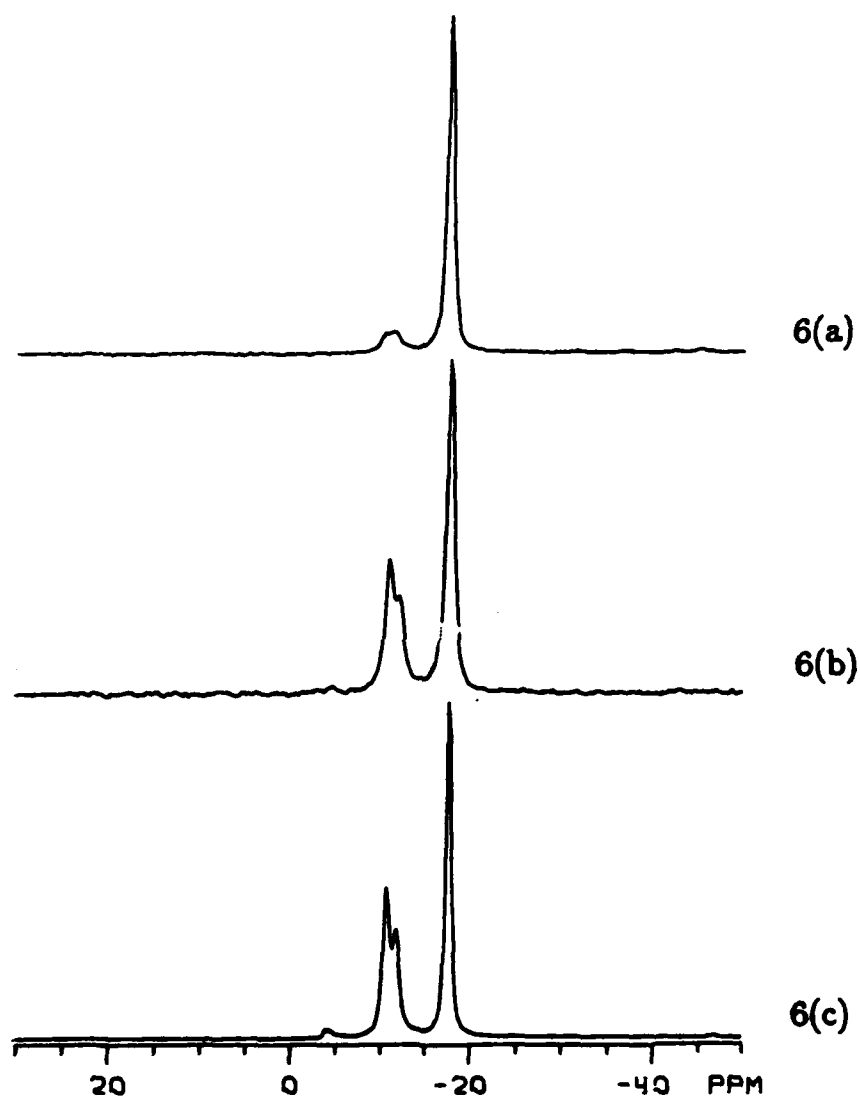


Figure 6. ^{31}P MAS NMR Spectra of PNBP Adsorbed on the Strong Acid Ion Exchange Resin: (a) 1 Day Old, Stored in a Capped 5mm NMR Tube; (b) 40 Days Old, Stored in a Capped 5mm NMR Tube; and (c) Same as (b) Except that the Sample was Left Exposed to Air for 6 Additional Days

PNPPA, based upon the solvent extraction and analysis of these products by solution NMR. The spectrum taken after the sample had been kept for 40 days in a capped 5mm NMR tube, 6(b), shows further hydrolysis of PNDP with DPPA apparently being the favored product. Solvent extraction of the strong acid resin yields the same relative amounts of PNDP, DPPA, and PNPPA in the filtrate, indicating that the products are easily removed and not tightly bound to the sulfonic acid ion exchange sites. Spectrum 6(c) was obtained from the same sample after it had been exposed to air for 6 days and shows further DPPA and PNPPA formation along with the appearance of a third peak at -4.4 ppm (product not identified). Even after long-term air exposure, the neutral acid products on the strong acid resin remain highly mobile and liquid like in the absence of coadsorbed ethanol, indicating an increased mobility of the neutral species as compared with the anionic base-catalyzed products.

5. CONCLUSIONS

³¹P Magic Angle Spinning NMR spectra of dimethyl methyl phosphonate (DMMP) adsorbed on the resin powder provide direct evidence for the partitioning of adsorbed organophosphorus ester occurring between two different adsorption sites. Comparison of spectra obtained for DMMP adsorbed on strong acid and strong base ion exchange resins and several carbonaceous adsorbents (similar to the three components of the resin powder) allows the assignment of the two adsorption sites to the reactive ion exchange resins and the carbonaceous adsorbent. Variable temperature spectra obtained for DMMP adsorbed on the resin powder indicate that DMMP exchange between the sites cannot be occurring at a rate greater than 300 s⁻¹.

The results obtained for the hydrolysis of p-nitrophenyl diphenyl phosphate (PNDP) adsorbed on the resin powder (from ethanol solution) reveal that the anionic diphenyl phosphate product appears to be tightly bound to the quaternary ammonium ion exchange sites. The PNDP diffusion is apparently much faster in the presence of coadsorbed ethanol, which greatly increases the rate of hydrolysis. Product immobilization does not occur for acid-catalyzed hydrolysis on the strong acid resin where the neutral diphenyl phosphoric acid and p-nitrophenyl phenyl phosphoric acid products remain highly mobile. However, the analogous acid-catalyzed process does not occur on the resin powder. The reason for the apparent lack of reactivity of the resin powder sulfonic acid groups remains unclear.

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