

constant, J_{PH_O} , is in the range observed in other arylphosphorus compounds.^{14,21} It is interesting to note that, although the difference is small, J_{PH_O} is lower for a geminal configuration at the phosphorus center than for a nongeminal configuration. A similar situation is observed in the dimethylaminochlorocyclotriphosphazenes.²² The origin of this difference could lie in the smaller bond angle (and hence less character) expected in a $\equiv\text{P}(\text{C}_6\text{H}_5)_2$ center compared to a $\equiv\text{PF}(\text{C}_6\text{H}_5)$ center.²³ However, due to the proximity of the ortho proton to the phosphorus atom, orbital and dipolar contributions may be significant factors in determining the

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magnitude of J_{PH_O} . Similar effects have been postulated for the tin-ortho proton coupling constants in phenyltin trihalides.²⁴

In conclusion, we have shown that examination of the proton nmr spectra of phenylcyclotriphosphazenes provides information concerning electronic interactions in these systems and could be a useful technique for establishing the presence and configuration of isomers in solution.

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Registry No. $\text{P}_3\text{N}_3\text{F}_2\text{C}_6\text{H}_3\text{D}_2$, 50859-00-2; 1,1- $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_3\text{D}_2)$ - (C_6H_2) , 50859-01-3; *cis*-1,3- $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_3\text{D}_2)_2$, 50859-02-4; *trans*-1,3- $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_3\text{D}_2)_2$, 50859-03-5; $\text{P}_3\text{N}_3\text{F}_2$ -1,3- $(\text{C}_6\text{H}_3\text{D}_2)_2$ -1,3- $(\text{C}_6\text{D}_5)_2$, 50932-73-5.

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Studies of Sulfur Imides in Basic Organic Solvents. Synthesis and Characterization of Tetra-*n*-butylammonium Perthionitrate, $(n\text{-C}_4\text{H}_9)_4\text{N}(\text{NS}_4)^-$ ¹

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Solutions of heptasulfur imide (S_7NH) in hexamethylphosphoramide (HMPA) are deep blue. The blue species has been isolated as the tetra-*n*-butylammonium salt and characterized as the NS_4^- anion. Infrared and Raman spectra suggest a branched chain structure. Solutions of S_7NH in dimethylformamide (DMF) contain both S_7N^- and NS_4^- in equilibrium; spectrometric and conductometric results were used to estimate the "aqueous" $\text{p}K_a$ (S_7NH) at 25° to be about 5 and to calculate the equilibrium constant for the reaction $\text{S}_7\text{N}^- \rightleftharpoons \text{NS}_4^- + \frac{3}{8}\text{S}_8$, $K_1 = 0.13 \pm 0.06$. Solutions of 1,4- $\text{S}_6(\text{NH})_2$ in HMPA slowly turn blue to give 1 mol of NS_4^- per $\text{S}_6(\text{NH})_2$.

Introduction

It has been known for many years that all the sulfur imides except tetrasulfur tetraimide give an intense blue coloration in basic organic solvents. This reaction is commonly used as a spot test in the chromatographic separation of the sulfur imides² and is dramatically apparent during their preparation from sulfur monochloride and ammonia in DMF. Lux and Anslinger suggested that the blue species formed by S_7NH in dimethyl sulfoxide (DMSO) was identical with that formed by alkali polysulfides in DMSO and erroneously attributed this color to neutral sulfur radicals, S_x ($x = 2-4$).³ Chapman and Massey reported that the blue species from S_7NH in DMSO is negatively charged but exhibits no esr signal; they suggested it is the S_7N^- anion.⁴ More recently Olsen and coworkers have carefully investigated the alkylation of sulfur imides under basic conditions. They were able to prove the existence of the S_7N^- anion in their blue tetrahydrofuran (THF) solutions but were unable to relate the color to any particular species.⁵ The sodium salt, Na-

S_7N , which had previously been isolated,⁶ is olive green. Finally, Mendelsohn and Jolly showed that in THF solution at -78° the S_7N^- anion is stable and yellow, but on warming above -40° it exists in equilibrium with the blue species which, therefore, is not *cyclo-S* $_7\text{N}^-$.⁷

We have reported that solutions of alkali polysulfides⁸ or elemental sulfur⁹ in HMPA are deep blue due to the presence of the S_3^- radical anion. We therefore decided to investigate the sulfur imides in HMPA, initially to determine if S_3^- is responsible for the color.

Experimental Section

Materials. HMPA (Aldrich) was dried with sodium hydride, stirred with sufficient potassium metal to turn the batch completely blue, vacuum distilled under nitrogen [bp 90° (4.7 mm); lit. bp 115° (15 mm) or 68° (1 mm)¹⁰], and then trickled through a column of freshly regenerated Linde 4A molecular sieves. DMF (Fisher) was degassed with a stream of nitrogen and then trickled through freshly regenerated Linde 4A molecular sieves. Purified solvents were stored and used in a dry oxygen-free atmosphere (Vacuum Atmospheres drybox). S_7NH was prepared from sulfur monochloride and am-

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monia in DMF by the literature method;² it was purified by chromatography on silica gel, which also yielded 1,4-S₆(NH)₂. The purified S₇NH had mp 113° (lit.² mp 113.5°) and was used for spectroscopic and conductometric measurements. S₇NH suitable for the preparative reactions was obtained by recrystallization of the crude reaction product from methanol. Tetra-*n*-butylammonium hydroxide (25% in methanol, Eastman) and all other chemicals were reagent grade and used as received.

Preparation of Tetra-*n*-butylammonium Perthionite

(*n*-C₄H₉)₄N(NS₄). Crude S₇NH (1.4 g, 5.85 mmol) was dissolved in anhydrous diethyl ether (150 ml) and the solution was filtered into a 250-ml three-necked flask. The solution was cooled to -80° under nitrogen and tetra-*n*-butylammonium hydroxide (7.5 ml of 25% solution in methanol, 7.25 mmol) in diethyl ether (12.5 ml) was added slowly. A greenish yellow precipitate formed. The solution was kept cold and filtered through a coarse glass frit attached to one neck of the flask. The greenish yellow solid on the frit was quickly transferred to the drybox and left for 3 days, when it had changed to a deep purple solid. An X-ray powder pattern revealed the presence of orthorhombic sulfur, α-S₈. Most of the sulfur was removed by Soxhlet extraction (in a fritted glass thimble) with dry *n*-hexane under nitrogen. Care must be taken not to allow the receiver to become too warm because of the low melting point of the product. Further purification was achieved by dissolving the dark blue solid in THF (10 ml), filtering, and allowing the THF to evaporate to give an oil. Addition of anhydrous diethyl ether (200 ml), in which the product is very sparingly soluble, precipitated a fine blue-black powder, mp 49°. Anal. Calcd for C₁₆H₃₆N₂S₄: C, 49.95; H, 9.43; N, 7.28; S, 33.34. Found: C, 50.20; H, 9.19; N, 7.12; S, 33.02. All manipulations of (*n*-C₄H₉)₄N(NS₄) were performed under a dry, oxygen-free atmosphere.

Physical Measurements. Conductivities were measured with a Beckman RC18 conductivity bridge operating at 1 kHz. Ultraviolet-visible spectra were obtained using a Beckman DBG spectrometer and infrared spectra with a Perkin-Elmer 337 instrument. Raman spectra were obtained using a Carson argon ion laser operating at 488.0 nm, with coaxial excitation and viewing with a Cary 81 spectrophotometer. For the electrical transference experiment a five-compartment cell with sintered-glass divisions between the compartments was used. The blue solution was placed in the central compartment and HMPA containing Bu₄NClO₄ in the other four compartments. A dc potential of 50 V was applied across the platinum electrodes in the two end compartments.

Results and Discussion

Synthesis and Visible Spectra of (*n*-C₄H₉)₄N(NS₄). S₇NH dissolves in HMPA to give an immediate intense blue color characterized by a broad absorption band with a smooth envelope λ_{max} 595 nm. There were no other maxima before the solvent cutoff at 260 nm. The blue species S₃⁻ is characterized by two absorption bands, one with fine structure at λ_{max} 620 nm and the other at λ_{max} 277 nm,⁸ and is thus not responsible for the color of sulfur imides in basic solvents. We confirmed the report⁴ that the blue species is anionic by electrical transference, and we could detect no paramagnetism by the nmr method.¹¹ The tetra-*n*-butylammonium salt of the blue species was isolated from the reaction of tetra-*n*-butylammonium hydroxide with S₇NH in diethyl ether at low temperatures. The dark blue solid obtained in this manner contains elemental sulfur, which can be removed by Soxhlet extraction with hexane to give (*n*-C₄H₉)₄N(NS₄). This salt had the same visible spectrum in either THF or HMPA as S₇NH in HMPA. Furthermore, the infrared spectrum of the solid (*vide infra*) was the same as the infrared spectrum of solutions of S₇NH in HMPA with sodium hydroxide present as base, indicating that it is the NS₄⁻ ion which is responsible for the blue color. Tetra-*n*-butylammonium perthionite does not obey Beer's law in either HMPA or THF solutions. At concentrations below ca. 1 × 10⁻⁵ M, ε(595) starts to decrease and a new peak appears at 470 nm, but at concentrations close to 1 × 10⁻⁴ M there is no sign of this second peak

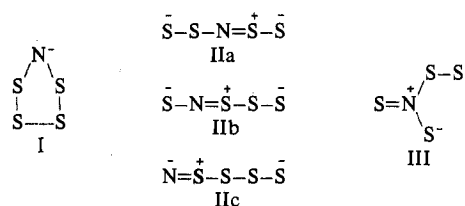
Table I. Vibrational Frequencies of NS₄⁻ (cm⁻¹)^a

I ^b		Raman ^c	Tentative
Nujol mull	HMPA soln	3 × 10 ⁻⁴ M in DMF	assignment ^d
		1157 m	2γ
		930 m	ν _a (NS ₃)
900 m	900 m	898 s	ν _b (NS ₃)
610 s	610 s		ν ₃ (NS ₃)
582, 575 s	580 vs	585 s	γ (NS ₃)
411 m			δ _a (NS ₃)
		355 m	δ _b (NS ₃)
303 w			ν (SS)

^a All values are ±5 cm⁻¹. ^b 250–4000 cm⁻¹. ^c 150–1500 cm⁻¹. ^d S. Pelloux and J. Roger, *C. R. Acad. Sci., Ser. C*, 270, 943 (1970).

and ε(595) is (1.90 ± 0.03) × 10⁴ M⁻¹ cm⁻¹.

Vibrational Spectra and Structural Assignment. A number of structures must be considered for the NS₄⁻ anion. These include cyclic (I), linear-chain (IIa, b, c), or branched-chain



(III) arrangements of the atoms. (Only one resonance form is shown in the valence bond representations of the unsaturated structures.) The vibrational frequencies of the NS₄⁻ ion are presented in Table I. The Raman spectrum exhibited a strong resonance enhancement and contained no lines attributable to the solvent or cation. The resonance effect is also responsible for the intensity of the first overtone band at 1157 cm⁻¹. In the infrared spectrum the bands due to the cation were determined by comparison with the spectrum of tetra-*n*-butylammonium perchlorate and the spectra of S₇NH in HMPA or DMF with sodium hydroxide present as base. The frequencies for the NS₄⁻ ion compare closely to those observed for the isoelectronic CS₄²⁻ ion,¹² and it is possible to assign all the frequencies on the basis of a branched structure (III), following the scheme outlined for CS₄²⁻.¹²

In an attempt to show that the NS₄⁻ anion contains only one S-S bond, as expected for structure III, a solution of the ion in THF was titrated with triphenylphosphine (ca. 8 × 10⁻³ M). After addition of 1 equiv of the phosphine, the solution was still royal blue; after addition of 2 equiv, the solution became green but returned to royal blue on standing for several hours. The blue color finally disappeared when 3.8 equiv of the phosphine had been added. Apparently there is a slow rearrangement of the initial reaction products, and the hypothetical NS₃⁻ ion is not stable under the conditions of the experiment.

Hydrolysis of (*n*-C₄H₉)₄N(NS₄). Since the NS₄⁻ ion is one of the major species present in the reaction mixture in the preparation of sulfur imides, we considered that hydrolysis of the pure anion might provide a high-yield route to sulfur di- and triimides. Accordingly a solution of (*n*-C₄H₉)₄N(NS₄) in THF (8 × 10⁻³ M) was hydrolyzed with 5% hydrochloric acid. The products were extracted with carbon disulfide, washed with water, and dried. Thin-layer chromatography shows the presence of elemental sulfur, S₇NH and S₆(NH)₂ isomers in approximately the same

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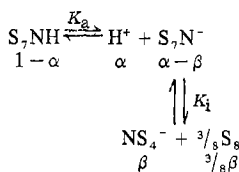
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distribution as from the usual preparation of sulfur imides.²

Formation of NS_4^- from $\text{S}_6(\text{NH})_2$ Isomers. 1,4- $\text{S}_6(\text{NH})_2$ dissolves in HMPA to give an initially pale blue solution due to the presence of NS_4^- , λ_{max} 595 nm. During 1 week this band grew to a maximum with $\epsilon(595)$ $1.88 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; i.e., 1 equiv of NS_4^- is produced per $\text{S}_6(\text{NH})_2$. Olsen and Tingle observed blue colors in the alkylation of 1,3-, 1,4-, and 1,5- $\text{S}_6(\text{NH})_2$ in THF-base, and they were mystified to isolate S_7NCH_3 , in addition to elemental sulfur and polysulfides, only in the case of the 1,3-diimide. From our observations it appears that the diimide anions can react to give NS_4^- which produces S_7N derivatives, e.g., on hydrolysis (*vide supra*). Moreover rearrangement of the anion derived from 1,4- $\text{S}_6(\text{NH})_2$ is a slow process and therefore 1,4- S_6N_2 derivatives are isolated from the alkylation reactions,^{5b} while the 1,3 isomer must rearrange quickly.

Formation of S_3^- from Sulfur Imides in HMPA. If redistilled HMPA is not treated with molecular sieves, it contains traces of dimethylamine which can reduce elemental sulfur to S_3^- .⁹ When S_7NH is dissolved in HMPA, which has not been degassed, the NS_4^- ion is still the immediate product, but over a period of 24 hr the band at 595 nm gives way to a structured band at 620 nm characteristic of S_3^- .⁸ Measurement of the intensity of this band gave values as high as 5.9 S atoms produced as S_3^- per S_7NH . A solution of S_7NCH_3 in untreated HMPA showed no trace of NS_4^- , but the S_3^- absorption band appeared immediately and grew steadily to a maximum value of 2.8 S atoms as S_3^- per S_7NCH_3 .

Acidity of S_7NH . Solutions of S_7NH in DMF deviate strongly from Beer's law at 595 nm. Since we know from previous work^{5a,7} that the S_7N^- ion is in equilibrium with another species, which is now shown to be NS_4^- , we can postulate the following equilibria for the DMF solutions



where

$$K_a = \frac{\alpha(\alpha-\beta)}{1-\alpha} [\text{S}_7\text{NH}] \qquad K_1 = \frac{\beta^{11/8}}{\alpha-\beta} [\text{S}_7\text{NH}]^{3/8}$$

and

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad \beta = \frac{\epsilon(595)}{\epsilon_0(595)}$$

and $[\text{S}_7\text{NH}]$ is the initial concentration of S_7NH . β is easily measured by calculating the ratio of $\epsilon(595)$ to the true extinction coefficient, $\epsilon_0(595)$, taken as $1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ from the measurements in HMPA. To estimate α , we assumed that the mobilities of the anions S_7N^- and NS_4^- are equal and measured the variation of conductivity with concentration. The experimental values are given in Table II. These values were smoothed graphically and Λ_0 was estimated by extrapolation. A series of values over the concentration range $(0.4\text{--}2.6) \times 10^{-4} \text{ M}$ were used to calculate α and β ; K_a and K_1 were then evaluated graphically, as shown in Figures 1 and 2, to give values of $(1.5 \pm 0.4) \times 10^{-5}$ and 0.13 ± 0.06 , respectively. This value of K_a refers to DMF solution; in order to compare the value with other acids it must be converted to the "aqueous" reference state by

Table II. Conductivities and $\epsilon(595)$ of Heptasulfur Imide in DMF

$10^4[\text{S}_7\text{NH}]$, <i>M</i>	$10^{-4}\epsilon(595)$, <i>M</i> ⁻¹ cm ⁻¹	$10^4[\text{S}_7\text{NH}]$, <i>M</i>	Λ , ohm ⁻¹ cm ² mol ⁻¹
0	1.90 ± 0.03	0	85 ± 3
0.155	1.58	0.39	61.5
0.293	1.36	0.75	58.3
0.792	1.14	1.31	47.3
1.55	0.816	1.93	39.4
1.98	0.686	2.74	32.8
2.93	0.502	3.59	28.7
		4.72	24.1

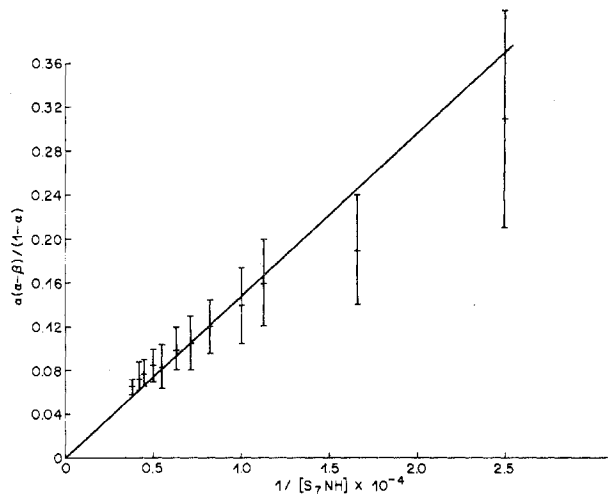


Figure 1. Variation of $\alpha(\alpha-\beta)/(1-\alpha)$ with $1/[\text{S}_7\text{NH}]$; slope = $K_a = (1.5 \pm 0.4) \times 10^{-5}$.

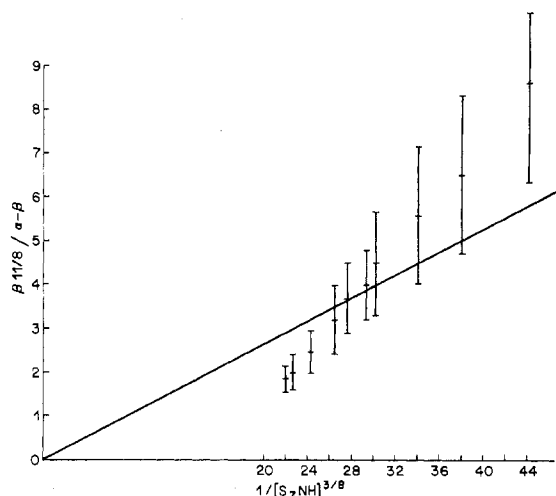


Figure 2. Variation of $\beta^{11/8}/(\alpha-\beta)$ with $1/[\text{S}_7\text{NH}]^{3/8}$; slope = $K_1 = 0.13 \pm 0.06$.

adding the $\text{p}K_a$ of protonated DMF in water. This value is -0.01 at 20° .¹³ The final $\text{p}K_a$ of S_7NH is around 5 indicating that it is about as strong as carboxylic acids. There are few compounds of known $\text{p}K_a$ with which to compare this value, but dialkylamines, e.g., piperidine $(\text{CH}_2)_5\text{NH}$, will have higher $\text{p}K_a$'s than ammonia which has $\text{p}K_a \approx 39$.¹⁴ Thus there is a remarkable factor of 10^{34} difference in the acidities of the N-H bond in NH_3 and S_7NH . We point out, however, that the bonding in sulfur-nitrogen compounds is not well understood, e.g., the S_2NH units in $\text{S}_4\text{N}_4\text{H}_4$ are

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planar,¹⁵ and it appears that sulfur-nitrogen anions are thermodynamically more stable than has generally been appreciated.

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Registry No. S_7NH , 293-42-5; $(n-C_4H_9)_4N(NS_4)$, 50859-28-4; $1,4-S_8(NH)_2$, 1003-76-5; S_8^- , 12597-04-5.

Contribution from the Research Resources Laboratory and the Department of Biological Chemistry, University of Illinois at the Medical Center, Chicago, Illinois 60612, and the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Structure and Properties of the Condensed Phosphates. XVIII. Ring-Chain and Other Equilibria in Organic Solvents

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Phosphoric acids in the range from the pyro- to the metaphosphate composition were equilibrated in selected mixtures of tetramethylurea and tri-*n*-butylamine and the resulting molecular distributions were measured by ^{31}P nmr. Cyclic molecules were found in much larger proportions than in any other phosphate system at the same cation:phosphorus ratio. Values of the equilibrium constants interrelating the variously sized ring and chain molecules are calculated and discussed.

Introduction

Although molecular equilibria involving the interconversion of cyclic structures of different sizes and the relation of these cyclic molecules to the noncyclics have been extensively studied both theoretically¹⁻³ and experimentally,⁴⁻⁸ little is known about this behavior for solutions of the condensed phosphoric acids and their salts, since most of the work reported for them has been done in water, which is a sufficiently reactive solvent so that hydrolysis competes with molecular reorganizations.⁹ It is true that the equilibria between phosphate molecule ions occurring in molten salts^{9,10} as well as in concentrated acids¹¹ have been profitably studied¹ using analytical procedures conducted in aqueous solution under conditions where hydrolysis was inconsequential. In the solvent-free systems where these equilibrations occurred, however, the close packing of the molecules involved in the redistribution reactions ensured the amount of cyclic phosphates was always quite small.

Attempts to conduct scrambling reactions to equilibrium do not work in aqueous solution because of the relatively

rapid hydrolysis of the condensed phosphates. By finding an appropriate nonaqueous solvent system for the condensed phosphate anions (using tertiary ammonium counterions to obtain reasonably high solubilities), it has been possible to carry out the work reported herein in which equilibrium with respect to phosphate scrambling was achieved in a nonreactive solvent at sufficient dilution so that cyclic molecules ought to predominate.

Experimental Section

Chemical Manipulations. Tetramethylurea from Eastman Organic Chemicals Co. was purified and carefully dried as previously described.¹² All of the other solvents were purified where necessary and rendered anhydrous by accepted procedures.¹³ The tri-*n*-butylamine which was used to make the ammonium phosphates in solution was also purified and dried according to the literature.¹² Although various combinations of phosphoric acids were occasionally employed as precursors in the equilibration studies, the usual procedure was to achieve the proper degree of condensation,¹² *D*, by adding water to commercial phosphorus pentoxide. To do this, the organic solvent containing the desired amount of amine was added to a 40-ml Teflon-capped centrifuge tube containing a weighed amount of P_2O_5 . After magnetic stirring to disperse the P_2O_5 , the amount of water needed to give the proper degree of condensation was added dropwise. Note that in order to determine the proper amount of added water, it was necessary to establish the water content of the P_2O_5 and this was achieved by precisely determining the degree of condensation of an equilibrated test mixture. Freshly opened bottles of phosphorus pentoxide were found to vary extensively in water content (from 0.01 to 5 wt % H_2O); however, if care is taken in dispensing (without use of drybox or drybag in the winter or with air conditioning), we find no change in the water content of the P_2O_5 in a 1-lb bottle being consumed over a period of several months.

All of the measurements reported in this paper correspond to equilibration at 62° for at least 4 weeks. Several studies of the rate of equilibration indicated that at this temperature there were no detectable changes in the ^{31}P nuclear magnetic resonance (nmr) patterns after 1 week in the slowest case. For those cases where phos-

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