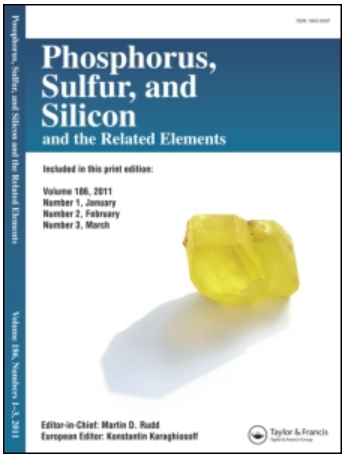


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CONDENSATION OF TETRAKIS(HYDROXYMETHYL)PHOSPHONIUM SULFATES AND SULFONATES WITH 1,3-DIMETHYLUREA

Arlen W. Frank[a]
[a] Southern Regional Research Center, New Orleans, Louisiana

To cite this Article Frank, Arlen W.(1981) 'CONDENSATION OF TETRAKIS(HYDROXYMETHYL)PHOSPHONIUM SULFATES AND SULFONATES WITH 1,3-DIMETHYLUREA', Phosphorus, Sulfur, and Silicon and the Related Elements, 10: 2, 207 — 212
To link to this Article: DOI: 10.1080/03086648108077507
URL: http://dx.doi.org/10.1080/03086648108077507

Phosphorus and Sulfur, 1981, Vol. 10, pp. 207–212
0308-664X/81/1002-0207$06.50/0

CONDENSATION OF TETRAKIS(HYDROXYMETHYL)PHOSPHONIUM SULFATES AND SULFONATES WITH 1,3-DIMETHYLUREA

ARLEN W. FRANK

Southern Regional Research Center[1], *New Orleans, Louisiana 70179*

(*Received August 4, 1980; in final form September 27, 1980*)

An unexpected displacement of one of the phosphorus groups occurred when the chloride **1a** was replaced by the sulfate **1b** in its reactions with 1,3-dimethylurea. The products, **2c** and **5c**, were bisulfates rather than sulfates. In contrast, no displacement occurred when **1a** was replaced by the sulfonates **1e** or **1f**. A method was developed for preparing the sulfonates **1d-h**, all new compounds, by metathesis of the sulfate **1b** with the appropriate barium sulfonate. The sulfates **2b** and **5b**, prepared from the chlorides **2a** and **5a** by ion exchange, yielded the bisulfates **2c** and **5c** upon treatment with sulfuric acid. The significance of the findings is discussed.

INTRODUCTION

Polymers prepared by condensing tetrakis(hydroxymethyl)phosphonium chloride $(HOCH_2)_4PCl$ (**1a**: THPC or TKC)[2], with nitrogen compounds such as urea or melamine are useful as flame retardant finishes for cotton.[3,4] In order to avoid the carcinogen bis(chloromethyl) ether, the textile industry has recently replaced **1a** by other tetrakis(hydroxymethyl)phosphonium salts such as the sulfate (**1b**: THPS or TKO), the oxalate (TKS), or the mixed phosphate-acetate (TKP).[5,6]

In a study of the reactions of tetrakis(hydroxymethyl)phosphonium salts with 1,3-dimethylurea, an unexpected displacement of one of the phosphorus groups occurred when **1a** was replaced by **1b**. The nature of this reaction and its significance are the subject of the present paper, coupled with the synthesis of a series of novel sulfonate salts and their 1,3-dimethylurea derivatives.

EXPERIMENTAL

Reagents

The sulfate **1b** was a commercial 75% THPS or 85% TKO solution. The sulfonate salts were prepared in situ by adding barium hydroxide or calcium hydroxide to an aqueous solution of the sulfonic acid, heating to 60°C, and filtering if necessary to remove impurities. Other reagents were used as obtained.

Methods

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared (IR) spectra were taken on a Perkin–Elmer 137B (w = weak, m = medium, s = strong, vs = very strong, br = broad). ^1H nuclear magnetic resonance (NMR) spectra were taken on a Varian A-60A or a Varian EM360L with TMS or DSS as an internal reference, ^{13}C NMR spectra on a Varian CFT-20 with dioxane as an internal reference (s = singlet, d = doublet, q = quartet, m = multiplet, br = broad).

The physical properties of all new compounds are listed in Table I and their spectroscopic data in Tables II and III.

Octakis(1,3-dimethylureidomethyl)diphosphonium sulfate (**2b**). A solution of the phosphonium chloride **2a**[7] (9.42 g, 0.02 mol) in water (25 ml) was passed onto a chromatographic column containing 50 g of Rexyn 201 (SO_4 form)[8] strong base anion exchange resin, and eluted with water until no more phosphonium salt passed through. The eluates (400 ml total), which gave negative tests for chloride with silver nitrate solution, were stripped under vacuum. The residue (10.74 g) was triturated with 2-propanol, filtered, and dried, giving 8.85 g (91.5%) of **2b** as a white crystalline solid, mp 147°C dec. An analytical sample, dried 4 h at 82°C/0.5 mm, analyzed as a dihydrate.

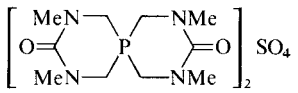
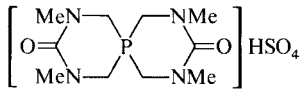
Anal. Calcd. for $C_{32}H_{72}N_{16}O_{12}P_2S.2H_2O$: C, 38.31; H, 7.64; N, 22.35; P, 6.17; S, 3.20. Found: C, 38.58; H, 7.89; N, 22.28; P, 6.17; S, 3.23.

The sulfate **2b** is soluble in water (pH 4.25, 0.1 *N* solution) and methanol and insoluble in other common organic solvents. Efforts to recrystallize the compound from ethanol, methanol/acetone, or other solvents were unsuccessful.

Tetrakis(1,3-dimethylureidomethyl)phosphonium hydrogen sulfate (**2c**). *A. From* **1b**. An 85% aqueous solution of **1b** (20.31 g, 0.05 mol) was refluxed with toluene (150 ml) in an oil bath with efficient stirring until no more water collected in a Dean–Stark trap. The mixture was cooled, treated with 1,3-dimethylurea (35.25 g, 0.40 mol), and heated again with efficient stirring until the evolution of water (7.4 ml, 0.41 mol) ceased (1 hr). The product, which had separated during the reaction as a mass of white solids, was triturated with 2-propanol, filtered, and dried, giving 31.05 g (116.6%) of **2c** as a white crystalline

TABLE I

Physical properties of new compounds

No.	Formula	Yield (%)	Mp (°C) or n_D^{20}
1d	$[(HOCH_2)_4P]SO_3Me$	99.3	1.5166
1e	$[(HOCH_2)_4P]SO_3C_6H_5$	97.6	63–64[a,b]
1f	$[(HOCH_2)_4P]SO_3C_6H_4Me$-p	101.6	60–61
1g	$[(HOCH_2)_4P]SO_3C_{10}H_7$-1	92.7	1.5902
1h	$[(HOCH_2)_4P]SO_3C_{10}H_7$-2	97.2	112–13[a]
2b	$[(MeNHCONMeCH_2)_4P]_2SO_4$	91.5	147 dec
2c	$[(MeNHCONMeCH_2)_4P]HSO_4$	116.6 (A) 83.4 (B)	177 dec
2e	$[(MeNHCONMeCH_2)_4P]SO_3C_6H_5$	73.9	103–05
2f	$[(MeNHCONMeCH_2)_4P]SO_3C_6H_4Me$-p	89.7	130–31
5b		82.6	177 dec
5c		65.8 (A) 95.1 (B)	206 dec
6f	$[(MeO_2CNHCH_2)_4P]SO_3C_6H_4Me$-p	92.9	1.5235

[a] Recrystallized from 1:3 2-propanol/ethyl acetate (4 ml/g).
[b] Calcd. for $C_{10}H_{17}O_7PS$: P, 9.92; S, 10.27. Found: P, 9.95; S, 10.26.

solid. Two recrystallizations from 2-propanol (30 ml/g), followed by 4 hr drying at 100°C/0.5 mm, gave pure **2c**, mp 177°C dec.

Anal. Calcd. for $C_{16}H_{37}N_8O_8PS$: C, 36.08; H, 7.00; N, 21.05; P, 5.82; S, 6.02. Found: C, 35.90; H, 7.16; N, 20.79; P, 5.70; S, 5.91.

The bisulfate **2c** is soluble in water (pH 1.20, 0.1 *N* solution), methanol, and Me_2SO and insoluble in other common organic solvents. It can also be recrystallized from ethanol (2 ml/g) or n-butanol (4 ml/g), forming 1:1 solvates that retain solvent tenaciously.

The presence of the acidic hydrogen was established by iodometric titration[9] to avoid hydrolysis of the phosphonium group. The sample (0.5 g) was weighed to four decimals, treated with water (10 ml) and potassium iodide (2.0 g), swirled until dissolved, treated with 0.1 *N* iodate (25.00 ml) and 0.1 *N* thiosulfate (25.00 ml), shaken overnight in a stoppered flask, and titrated with 0.1 *N* iodine to a blue end point with starch indicator. Calcd.: MW, 532.6. Found: MW 539, 542.

The 2-propanol-soluble fraction yielded 17.40 g of yellow oil that gave a positive test for P(III) with iodine.

The results were identical whether the condensation was carried out with THPS or TKO.

B. From **2b**. A solution of **2b** (2.006 g, 2 mmol) in water (5 ml) was treated with 10% sulfuric acid (2.00 g, 2 mmol), shaken briefly, and stripped under vacuum. The residue was triturated with 2-propanol, filtered, and dried, giving 1.776 g (83.4%) of **2c**, mp 176°C dec, identical (IR, ^1H NMR) to the product obtained from **1b**.

TABLE II

IR spectroscopic data for new compounds, cm^{-1}

No.	Phase	Vibrations
1d	Neat	νOC 1030s and 1175 vs, νOH 3230s
1e	Nujol	δC_6H_5 685m, 730m and 752m, νOC 1030s and 1180vs, νOH 3220s
1f	Nujol	δp-tolyl 768w and 807m, νOC 1030vs and 1170vs, νOH 3230vs
1g	Neat	δ1-$C_{10}H_7$ 767m, νOC 1030vs and 1175vs, νOH 3230vs
1h	Nujol	δ2-$C_{10}H_7$ 747m, νOC 1020vs and 1175s, νOH 3240vs, and 1075s
2b	KBr	νNH 1525s and 3330s, νC = O 1620vs, νSO_4 1110s
2c	KBr	νNH 1540s and 3340s, νC = O 1625vs, νHSO_4 1050m and 1180m
2e	Nujol	δC_6H_5 686w, 726m and 750w, νNH 1540vs and 3300s, νC = O 1640vs
2f	Nujol	δp-tolyl 770w and 816w, νNH 1540vs and 3310s, νC = O 1625vs
5b	KBr	νC = O 1650vs, νSO_4 1100–30vs
5c	KBr	νC = O 1655vs, νHSO_4 1050s and 1155s
6f	Neat	δp-tolyl 775m and 817m, νNH 1510s and 3300s, νC = O 1700vs

TABLE III

^{1}H NMR spectroscopic data for new compounds, δ ppm, J Hz

No.	Solvent	$\delta_{CH_2}(J_{PH})$	Other signals
1d	D_2O	4.66d (1.5)	δCH_3 2.78s
1e	D_2O (60°C)	4.70d (2.5)	δC_6H_5 7.43–7.75m (m- and p-H) and 7.75–7.80m (o-H)[a]
1f	Me_2CO-d_6	4.77s br	δCH_3 2.34s, δOH 5.68s br, vanishing with D_2O, δC_6H_4 7.28 (m-H) and 7.78 (o-H)[b]
1g	D_2O	4.72d (1.5)	$\delta C_{10}H_7$ 7.35–8.35m (2- to 7-H) and 8.86d br (8-H, 9.0 Hz)[c]
1h	D_2O	4.73d (2.0)	$\delta C_{10}H_7$ 7.43–8.10m (3- to 8-H) and 8.38s br (1-H)[d]
2b	D_2O	3.93d (4.0)	δ3-CH_3 2.74s, δ1-CH_3 3.00d (1.5)
2c	Me_2SO-d_6	3.78d (4.5)	δ3-CH_3 2.61d (4.0), collapsing to s with D_2O, δ1-CH_3 2.93d (1.5), δOH 6.87d br (5), vanishing with D_2O
2e	D_2O	3.89d (4.0)	δ3-CH_3 2.72s, δ1-CH_3 2.95d (2.0), δC_6H_5 7.23–7.65m (m- and p-H) and 7.65–7.90 m(o-H)[a]
2f	D_2O	3.92d (4.0)	δp-CH_3 2.39s, δ3-CH_3 2.75s, δ1-CH_3 2.97d (1.5), δC_6H_4 7.37 (m-H) and 7.73 (o-H)[b]
5b	D_2O	4.40d (8.0)	δCH_3 2.97d (2.5)
5c	D_2O	4.38d (8.0)	δCH_3 2.97d (2.0)
6f	D_2O	4.32d (4.0)	δp-CH_3 2.36s, δOCH_3 3.72s, δC_6H_4 7.31 (m-H) and 7.68 (o-H)[b]

[a] Assignments based on benzenesulfonic acid[13h] and its barium salt.[13h]
[b] Extracted from AA'BB' multiplet; assignments based on p-toluenesulfonic acid[13c] and its barium salt.[13e]
[c] Assignments based on 1-naphthalenesulfonic acid[13f,g] and its potassium salt.[13j]
[d] Assignments based on 2-naphthalenesulfonic acid[13d] and its sodium salt.[13a]

Tetrakis(1,3-dimethylureidomethyl)phosphonium chloride (**2a**). Addition of barium chloride (3.16 g, 15 mmol) in water (25 ml) to a solution of the bisulfate **2c** (5.33 g, 10 mmol) in water (25 ml) caused an immediate separation of solids. The mixture was boiled briefly, cooled, and filtered, giving 2.35 g (10.1 mmol) of barium sulfate. The filtrate, stripped and extracted with 2-propanol, yielded 1.03 g (4.9 mmol) of barium chloride. The extract was stripped, neutralized with aqueous sodium bicarbonate, and recrystallized from 2-propanol, giving 2.48 g (52.7%) of a white crystalline solid, mp 191–192°C dec, identified as **2a** by IR and ^{1}H NMR.[7]

Tris(1,3-dimethylureidomethyl)phosphine oxide (**4**). The bisulfate **2c** (5.33 g, 10 mmol) was added in portions to a solution to sodium hydroxide (0.80 g, 20 mmol) in water (25 ml). Each portion was allowed to dissolve before adding the next. The solution was then boiled briefly, cooled, and stripped to dryness in a rotary evaporator. The residue was digested with methanol (25 ml), filtered to remove sodium sulfate, stripped under vacuum, digested with chloroform (25 ml) to remove 1,1,3-trimethylurea (0.59 g, 58% yield, mp 60–65°C, identified by IR), and stripped again, giving 3.61 g (103%) of a white crystalline solid, mp 220–22°C dec, identified as **4** by IR and ^{1}H NMR.[7]

The ^{13}C NMR spectrum of **4** in D_2O showed signals at δ 28.0 (s, 3-CH_3), 37.2 (s, 1-CH_3), 47.6 (d, CH_2, J_{PC} 64.5 Hz), and 161.3 (s, C = O) ppm. The 3-CH_3 assignment was based on the spectra of N-methylurea and 1,3-dimethylurea.

Bis(3,9 - dioxo - 2,4,8,10 - tetramethyl - 2,4,8,10 - tetraaza - 6 - phosphoniaspiro[5.5]undecane) sulfate (**5b**). A solution of the spiro phosphonium chloride **5a**[10] (5.89 g, 0.02 mol) in water (25 ml) was percolated through Rexyn 201 (SO_4 form) resin, as described above for **2a**, giving 5.08 g (82.6%) of **5b** as a white crystalline solid, mp 177°C dec (reddening). An analytical sample, dried 4 h at 82°C/0.5 mm, analyzed as a hydrate.

Anal. Calcd. for $C_{20}H_{40}N_8O_8P_2S.H_2O$: C, 37.97; H, 6.69; N, 17.72; P, 9.79; S, 5.07. Found: C, 38.03; H, 6.86; N, 17.30; P, 9.67; S, 5.17.

The sulfate **5b** is soluble in water (pH 2.55, 0.1 *N* solution) and methanol and insoluble in other common organic solvents.

3,9 - Dioxo - 2,4,8,10 - tetramethyl - 2,4,8,10 - tetraaza - 6 - phosphoniaspiro[5.5] undecane hydrogen sulfate (**5c**). *A. From* **1b**. Condensation of **1b** (20.31 g, 0.05 mol) with 1,3-dimethylurea (17.62 g, 0.20 mol) under the conditions described above for **2c** gave 11.72 g (65.8%) of **5c** as a white crystalline solid, mp 206°C dec after recrystallization from dimethylformamide (24 ml/g).

Anal. Calcd. for $C_{10}H_{24}N_4O_6PS$: C, 33.70; H, 5.94; N, 15.73; P, 8.69; S, 9.00. Found: C, 33.53; H, 6.26; N, 15.66; P, 8.57; S, 8.84.

The bisulfate **5c** is soluble in water (pH 1.45, 0.1 *N* solution) and insoluble in all common organic solvents.

The 2-propanol-soluble fraction yielded 13.13 g of yellow oil that gave a positive test for P(III) with iodine. Its ^{1}H NMR spectrum (D_2O) showed signals at δ 2.71 (s, 3H, $NHCH_3$), 2.85–2.97 (m, 6H, NCH_3), and 3.33–4.25 (m, 6H, CH_2) ppm.

B. From **5b**. A solution of **5b** (1.265 g, 2 mmol) in water (5 ml) was treated with 10% sulfuric acid (2.00 g, 2 mmol), shaken briefly, and stripped under vacuum. The residue was triturated with 2-propanol, filtered, and dried, giving 1.355 g (95.1%) of **5c**, mp 204°C dec (reddening), identical (IR, ^{1}H NMR) to the product obtained from **1b**.

Tetrakis(hydroxymethyl)phosphonium sulfonates (**1d-h**). A 75% aqueous solution of **1b** (203.13 g, 0.5 mol) was added slowly to a

hot solution of barium p-toluenesulfonate (239.86 g, 0.5 mol) in water (1500 ml), causing an immediate separation of solids. The mixture was heated briefly to 80°C to digest the precipitate, allowed to cool slowly, and filtered, giving 118.93 g (101.9%) of barium sulfate.[11] The filtrate was stripped under reduced pressure, azeotroped with benzene to remove the residual water, stripped again, slurried with acetone, and filtered, giving 6.39 g (2.7%) of white flakes, mp > 270°C, identified by IR[12] and ^{1}H NMR[13e] as barium p-toluenesulfonate. The filtrate, stripped under vacuum, yielded 341.45 g (101.6%) of tetrakis(hydroxymethyl)phosphonium p-toluenesulfonate (**1f**) as a grayish oil that crystallized when rubbed. A portion of the product was recrystallized from 2-propanol (1 ml/g), giving a hygroscopic white solid, mp 60–61°C (sealed tube).

Anal. Calcd. for $C_{11}H_{19}O_7PS$: C, 40.49; H, 5.87; P, 9.49; S, 9.83. Found: C, 40.56; H, 5.90; P, 9.50; S, 9.61.

The phosphonium salt **1f** is soluble in water, ethanol, acetone, and acetonitrile and insoluble in chloroform, carbon tetrachloride, and ether.

The other sulfonates were prepared in the same manner, except for the use of 2-propanol instead of acetone in the workup of **1d** and **1g**. For textile applications, the synthesis of **1e** was scaled up fivefold without difficulty, with calcium benzenesulfonate prepared from technical grade benzenesulfonic acid. The products are all hygroscopic except **1h**.

Tetrakis(1,3 - dimethylureidomethyl)phosphonium sulfonates (**2e,f**). A mixture of the p-toluenesulfonate **1f** (16.31 g, 0.05 mol), 1,3-dimethylurea (17.62 g, 0.20 mol), and toluene (200 ml) was heated to reflux in a flask fitted with a mechanical stirrer and a Dean–Stark trap for azeotropic removal of the water. After 1 hr at reflux, the evolution of water (3.6 ml, 0.2 mol) ceased. The toluene layer was decanted, and the product, a heavy oil, was rubbed with acetonitrile, filtered, and rinsed with acetonitrile, giving 27.21 g (89.7%) of tetrakis(1,3 - dimethylureidomethyl)-phosphonium p-toluenesulfonate (**2f**) as a white crystalline solid, mp 130–131°C after two recrystallizations from acetonitrile. An analytical sample was dried at 100°C/0.5 mm for 2 hr.

Anal. Calcd. for $C_{23}H_{43}N_8O_7PS$: C, 45.53; H, 7.14; N, 18.47; P, 5.10; S, 5.28. Found: C, 45.19; H, 7.47; N, 18.25; P, 5.06; S, 5.15.

The phosphonium salt **2f** is soluble in water, ethanol, Me_2SO, and dimethylformamide and insoluble in most other organic solvents. It can be recrystallized from acetonitrile (40 ml/g) or 2-propanol (9 ml/g), separating from both in the form of solvates, mp 143–145°C, that retain solvent tenaciously.

The benzenesulfonate **2e**, prepared in the same manner, was a white crystalline solid, mp 103–105°C after three recrystallizations from acetonitrile (3 ml/g). A sample, dried at 56°C/0.5 mm for 3 hr, analyzed as a hydrate.

Anal. Calcd. for $C_{22}H_{41}N_8O_7PS.H_2O$: C, 43.26; H, 7.10; N, 18.35; P, 5.07; S, 5.25. Found: C, 43.69; H, 7.46; N, 18.31; P, 5.11; S, 5.21.

Tetrakis(N-carbomethoxylaminomethyl)phosphonium p-toluenesulfonate (**6f**). A mixture of the p-toluenesulfonate **1f** (16.31 g, 0.05 mol), methyl carbamate (15.01 g, 0.2 mol), and toluene (200 ml) was heated to reflux in a flask fitted with a mechanical stirrer and a Dean–Stark trap for azeotropic removal of the water. After 2 hr at reflux, the evolution of water (3.6 ml, 0.2 mol) ceased. The toluene layer was decanted, and the product, a heavy oil, was taken up in acetonitrile, filtered, and stripped under vacuum, giving 25.75 g (92.9%) of **6f** as a yellow oil, n_D^{20} 1.5235.

Tetrakis(N - carbomethoxylaminomethyl)phosphonium chloride (**6a**). A solution of the p-toluenesulfonate **6f** (5.54 g, 0.01 mol) in water (20 ml) was passed onto a chromatographic column containing 50 g of Bio-Rad AG50W-X4 cation exchange resin[14] and eluted with water (500 ml). A small quantity (8.1%) of the **6f** passed through, together with the p-toluenesulfonic acid (1.44 g, 83.6%). The products were separated by stripping, drying, and extracting the p-toluenesulfonic acid from the residue with ether. The column was then eluted with 3 *N* HCl (500 ml), giving 3.75 g (89.5%) of a white crystalline solid, mp 187–87.5°C dec, identified as **6a** by IR and ^{1}H NMR.[14]

RESULTS

Condensation of **1b** (THPS or TKO) with 1,3-dimethylurea in refluxing toluene with azeotropic removal of the water, as described previously[7] for **1a** (THPC), gave a white crystalline solid, mp 177°C dec, similar in appearance and physical properties to the compound **2a** obtained from **1a** but containing only one phosphorus per sulfur. The remainder of the product was a yellow oil. The probable stoichiometry of the reaction is given in Eq. 1:

$$[(HOCH_2)_4P]_2SO_4 + 8(MeNH)_2CO \longrightarrow [(MeNHCONMeCH_2)_4P]HSO_4 + \{(MeNHCONMeCH_2)_3P + CH_2O + (MeNH)_2CO\} + 7H_2O \quad (1)$$

(**1b** → **2c**; **3**)

The crystalline product, **2c**, was a bisulfate rather than a sulfate. The presence of an acidic hydrogen was established by iodometric titration. The identity of the product was confirmed by hydrolysis with sodium hydroxide to the tertiary phosphine oxide **4** and 1,1,3-trimethylurea and by metathesis with barium chloride to the phosphonium chloride **2a**. Both **4** and **2a** are known compounds.[7]

The oily product, represented by the compounds within braces, was an intractable mixture. A positive iodine test provided evidence for P(III), but efforts to isolate the tertiary phosphine **3** from the mixture were unsuccessful.

When the ratio of 1,3-dimethylurea to **1b** was reduced from 8:1 to 4:1, the condensation product was a white crystalline solid, mp 206°C dec, similar to the spiro phosphonium chloride **5a** obtained from **1a**[10] but containing one phosphorus per sulfur. This product (**5c**) was also a bisulfate (Table I).

The diphosphonium sulfates **2b** and **5b** were prepared from the corresponding phosphonium

chlorides **2a**[7] and **5a**[10] by ion exchange. The products were white crystalline solids, mp 147°C dec and 178°C dec, respectively. The ^{1}H NMR spectra of each pair were indistinguishable, but the IR spectra of the sulfates showed a strong absorption band in the 1080–1125 cm^{-1} region (asym. SO_4 stretching) that was absent in the bisulfates. The assignments, given in Table II, resemble those of inorganic salts.[15]

Treatment of the diphosphonium sulfates **2b** and **5b** with sulfuric acid in a 1:1 molar ratio gave the phosphonium bisulfates **2c** and **5c** in 83.4 and 95.1% yield, respectively. The identities of the products were confirmed by mp, IR, and ^{1}H NMR.

Condensation of tetrakis(hydroxymethyl)phosphonium *p*-toluenseulfonate (**1f**) with 1.3-dimethylurea under the same conditions gave a crystalline product, mp 130–31°C, in 89.7% yield. The product was identified as **2f** by IR, NMR, and elemental analysis. The benzenesulfonate **1e** reacted similarly, giving **2e**, mp 103–05°C, in 73.9% yield. There was no displacement of phosphorus groups in either condensation. The stoichiometry was the same as for the condensation of 1,3-dimethylurea with **1a** (Eq. 2):

$$\underset{\mathbf{1}}{[(HOCH_2)_4P]X} + 4(MeNH)_2CO \longrightarrow \underset{\mathbf{2}}{[MeNHCONMeCH_2)_4P]X} + 4H_2O \quad (2)$$

a, X = Cl
e, X = $SO_3C_6H_5$
f, X = $SO_3C_6H_4Me$-*p*

Condensation of the *p*-toluenesulfonate **1f** with methyl carbamate under the conditions employed with **1a**[14] and **1b**[16] gave a viscous yellow oil characterized as **6f** (Eq. 3) by IR, ^{1}H NMR, and by conversion to the phosphonium chloride **6a**, a known compound[14] by ion exchange.

$$\underset{\mathbf{1}}{[(HOCH_2)_4P]X} + 4MeO_2CNH_2 \longrightarrow \underset{\mathbf{6}}{[(MeO_2CNHCH_2)_4P]X} + 4H_2O \quad (3)$$

a, X = Cl
f, X = $SO_3C_6H_4Me$-*p*

The tetrakis(hydroxymethyl(phosphonium sulfonates required for these condensations were prepared by metathesis of the sulfate **1b** with the appropriate barium sulfonate (Eq. 4):

$$\underset{\mathbf{1b}}{[HOCH_2)_4P]_2SO_4} + BaX_2 \longrightarrow \underset{\mathbf{1d\text{–}h}}{2[HOCH_2)_4P]X} + BaSO_4 \quad (4)$$

d, X = SO_3Me
e, X = $SO_3C_6H_5$
f, X = $SO_3C_6H_4Me$-*p*
g, X = $SO_3C_{10}H_7$-1
h, X = $SO_3C_{10}H_7$-2

The reaction was carried out at 60°C or above to minimize coprecipitation of the product with the barium sulfate. After digestion and filtration, the product was separated from unreacted barium sulfonate by extraction with acetone or 2-propanol. Calcium sulfonates are preferred for large-scale preparations such as those needed for textile wet finishing.

DISCUSSION

The behavior of **1b** toward 1,3-dimethylurea can be understood in terms of the following dissociation (Eq. 5):

$$\underset{\mathbf{1b}}{[(HOCH_2)_4P]_2SO_4} \rightleftharpoons \underset{\mathbf{1c}}{[(HOCH_2)_4P]HSO_4} + \underset{\mathbf{7}}{(HOCH_2)_3P} + CH_2O \quad (5)$$

Condensation of 1,3-dimethylurea with **1b** to give the diphosphonium sulfates **2b** and **5b**, followed by hydrolysis in the hot reaction mixture to **2c** and **5c**, respectively, was ruled out because the hydrolysis by-products should be tertiary phosphine oxides rather than tertiary phosphines.[7,10] Condensation obviously occurs with the dissociation products rather than with **1b** itself. Reaction of 1,3-dimethylurea with **1c** gives either **2c** or **5c** directly, depending on the molar ratio. Reaction of 1,3-dimethylurea with tris(hydroxymethyl)phosphine (**7**) produces intractable oils,[17] and is further complicated by the release of formaldehyde, which can interact with the product **3** and with the 1,3-dimethylurea to give more highly substituted products, as it does with the carbamate derivatives.[14]

To what extent, then, do the dissociation products of Eq. (5) represent the structure of THPS? Anhydrous THPS is a hygroscopic oil, liquid at room temperature but solid at −42°C.[8]

Its reported phosphorus content,[18] neutralization equivalent,[19] iodine titer,[19] and gasometric assay[8] all support structure **1b**. The pH and iodine titer of 75% THPS were unchanged after a 4 hr reflux in an oil bath. The vapors above the boiling liquid gave a positive test for phosphine (PH_3) with moistened silver nitrate paper, but **1a**, whose stability is unquestioned, exhibits the same behavior.[20] Clearly, **1b** does not dissociate by itself to any significant extent.

In order for the reaction of 1,3-dimethylurea with the dissociation products of **1b** to proceed, the equilibrium must be shifted to the right, either by selective reaction with one or more of the dissociation products (**1c** and **7**), or by promoting the dissociation of the **1b**.

The base strength of the 1,3-dimethylurea must be a factor, because less basic reagents such as urea or methyl carbamate react with **1b** to give sulfates rather than bisulfates.[16,21] More basic ureas, such as 1,1,3-trimethylurea, degrade even the chloride **1a**.[7,22]

The acid strength of **1b** must also be a factor, because the sulfonates **1e, f** do not exhibit this behavior. The sulfonic acids all have pK_a values in the 0 ± 1 range,[23,24] whereas sulfuric acid has pK_a values of -3 and 2.0.[24] Behavior toward 1,3-dimethylurea similar to **1b** should be exhibited by other tetrakis(hydroxymethyl)phosphonium salts derived from acids of $pK_a \geq 2$, such as the acetate, phosphate, or oxalate.

The behavior of tetrakis(hydroxymethyl)phosphonium salts toward ureas, carbamates, and other reagents therefore depends on both the strength of the acid from which the phosphonium salt is derived and the base strength of the other reagent.

ACKNOWLEDGMENTS

I thank Gordon J. Boudreaux and Andrew G. Pierce, Jr. for the ^{31}P and ^{13}C NMR spectra and Jacqueline M. Simoneaux for some of the experimental work.

REFERENCES AND NOTES

1. One of the facilities of the Southern Region, Science and Education Administration, U.S. Department of Agriculture.
2. Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.
3. W. A. Reeves, G. L. Drake, Jr., and R. M. Perkins, *Fire Resistant Textiles Handbook* (Technomic Publishing Co., Inc., Westport, Conn., 1974), pp. 84–110.
4. J. W. Lyons, *The Chemistry and Uses of Fire Retardants* (Wiley-Interscience, New York, N.Y., 1970), pp. 189–208.
5. THPC and THPS: Hooker Chemicals and Plastics Corp., Niagara Falls, N.Y.
6. *Pyroset* TKC, TKO, TKP, and TKS: American Cyanamid Co., Bound Brook, N.J.
7. A. W. Frank, *Phosphorus Sulfur*, **5**, 19 (1978).
8. S. E. Ellzey, Jr., *Text. Chem. Color.*, **10**(5), 12 (1978).
9. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis* (Macmillan, New York, N.Y., 1943), rev. ed., p. 616.
10. A. W. Frank, *Phosphorus Sulfur* **10**, 147 (1981).
11. Filtration is slow but can be hastened by a filter aid such as Celite.
12. *Sadtler Infrared Prism Spectra* (Sadtler Research Laboratories, Philadelphia, Pa.), No. 23,707.
13. *Sadtler Standard NMR Spectra* (Sadtler Research Laboratories, Philadelphia, Pa.), a) No. 6,161. b) No. 9,509. c) No. 10,259. d) No. 10,947. e) No. 14,422. f) No. 19,095. g) No. 23,861. h) No. 27,276. j) No. 27,999.
14. A. W. Frank and G. L. Drake, Jr., *J. Org. Chem.*, **42**, 4040 (1977).
15. N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press, New York, N.Y., 1964), p. 310.
16. A. W. Frank, *Can. J. Chem.*, **59**, 27 (1981).
17. A. B. Pepperman, Jr., D. J. Daigle, and S. L. Vail, *J. Org. Chem.*, **41**, 675 (1976).
18. G. Hooper, W. N. Nakajima, and K. J. Remley, *Proc. Symp. Text. Flammability*, 3rd, 248 (1975).
19. J. P. Moreau, J. F. Seal, and J. V. Beninate, *J. Fire Retard. Chem.*, **5**, 73 (1978).
20. A. W. Frank and G. L. Drake, Jr., *J. Org. Chem.*, **36**, 549 (1971).
21. D. J. Daigle, A. W. Frank, and R. M. H. Kullman, *J. Fire Retard. Chem.*, **6**, 276 (1979).
22. A. W. Frank and D. J. Daigle, *Phosphorus Sulfur*, in press.
23. C. H. Rochester, *Acidity Functions* (Academic Press, New York, N.Y., 1970), pp. 57–58, 65.
24. A. Albert and E. P. Serjeant, *Ionization Constants of Acids and Bases* (Wiley, New York, N.Y., 1962), pp. 131, 151.