

## Use of Aldehydes Other Than Formaldehyde in THPOH/Ammonia Flame-Retardant Finishes for Cotton

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### Synopsis

Several aldehydes have been tested as substitutes for the lachrymator formaldehyde in the THPOH/ammonia process. Aldehydes such as acetaldehyde or butyraldehyde promote rapid polymer formation without being incorporated into the finish. Chloral is incorporated to a limited extent, but the finish is sensitive to base. To gain further insight into the polymer-forming process, the reactions of THP and its aldehyde derivatives with ammonia have been investigated in vitro. There is evidence that THP acts as a difunctional reagent, regardless of the aldehyde, forming a linear polymer with a single phosphorus, nitrogen, and oxygen atom in each repeating unit.

### INTRODUCTION

The THPOH/ammonia process, one of several developed in recent years for applying flame-retardant finishes to cotton,<sup>1c</sup> consists of padding fabric through a concentrated aqueous solution of tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH), drying to a moisture content of about 10%, and curing with ammonia vapor at room temperature in a closed chamber. The ammonia reacts with the THPOH, depositing a highly insoluble polymer within the fiber.<sup>2,3</sup>

One problem associated with this process is the irritating odor of formaldehyde, a lachrymator, released from the THPOH during padding and drying.<sup>4,5</sup> Methods proposed to overcome this problem include the use of less sodium hydroxide for neutralizing the tetrakis(hydroxymethyl)phosphonium chloride (Thpc) to inhibit formation of formaldehyde<sup>5,6</sup> and the use of sodium sulfite in place of all or part of the sodium hydroxide to tie up the formaldehyde as its bisulfite addition compound.<sup>5,7</sup> These methods have a common disadvantage—formaldehyde is a necessary ingredient in the polymer-forming reaction<sup>8</sup>—and efforts to suppress one inevitably tend to suppress the other. In this paper, we shall explore the possibility of replacing formaldehyde in this process with a different aldehyde.

\* A preliminary account of this work was presented at the Southeast-Southwest Combined Regional Meeting, American Chemical Society, New Orleans, La., Dec. 4, 1970.

## EXPERIMENTAL

### Reagents

Tris(hydroxymethyl)phosphine (THP), analyzing 0.08%  $\text{CH}_2\text{O}$  by the dime-done method,<sup>9</sup> was prepared by passing phosphine through 37% formalin solution, with cadmium chloride as the catalyst, until no more phosphine was absorbed.<sup>10</sup> For this work it was essential that the reaction be complete, for even small amounts of formaldehyde obscured the effect of other aldehydes on THP. Completion of the reaction was signaled by a drop in pH from 9 to 7. THP is deliquescent, but is stable to air for short periods. Its infrared spectrum showed no noticeable increase in  $\text{P}=\text{O}$  absorption after 4 hr of exposure to dry air in a desiccator or to humid air on the refractometer plates, but its refractive index ( $n_D^{25}$ , supercooled) dropped from 1.5564 to 1.5491 in 5 min, and to 1.5353 in 4 hr. Prolonged exposure to air should, of course, be avoided.

The aldehydes were reagent-grade products and were used as obtained, except for butyraldehyde, which was redistilled.

### Reaction of THP with Aldehydes

A 3.0-g sample of THP, weighed to four decimals and analyzing 16.46 mmole THP by iodometric titration,<sup>11</sup> was treated under nitrogen with acetaldehyde in several portions over a 4-hr period at 0–10°C. The mixture was allowed to warm to room temperature between additions. The THP dissolved slowly, with no noticeable exotherm. After evaporation overnight under a slow nitrogen flow, there remained a colorless oil with a sharp odor. The increase in weight corresponded to 33.72 mmole acetaldehyde, the ratio being 2.05:1 with respect to the THP. The product, Ia, showed weak absorption in the carbonyl region of the infrared, but very strong absorption at 3400 (O—H) and 1010 (C—O)  $\text{cm}^{-1}$ . Prolonged evacuation of Ia in a vacuum desiccator over phosphorus pentoxide removed half of the acetaldehyde in two days, leaving 16.15 mmole, or 0.92:1 with respect to the THP. This product, Ib, was a colorless oil,  $n_D^{25}$  1.5248, still having a sharp odor and an infrared spectrum similar to that of Ia. The product was soluble in water and ethanol, and insoluble in other common organic solvents. Its titer (as THP) was unchanged, since acetaldehyde does not interfere with the iodometric method used.<sup>11</sup>

Butyraldehyde also formed a 2:1 adduct with THP. In this case, the reaction mixture was heated at reflux for 15 min and then stripped under water pump vacuum for 15 min at 70° to remove the excess aldehyde. The product, II, was a viscous, colorless oil showing very weak absorption at 1700 (C=O)  $\text{cm}^{-1}$  in the infrared and very strong absorption at 3400 (O—H) and 1010 (C—O)  $\text{cm}^{-1}$ .

When these reactions were carried out in a glacial acetic acid as reactant and solvent, the THP dissolved at once with an exotherm. The infrared spectra of the phosphonium acetates,  $[(\text{HOCH}_2)_3\text{PCH}(\text{OH})\text{R}]\text{OAc}$  (R = Me or Pr), showed strong absorption at 3350 (O—H) and 1700 (acetate C=O)  $\text{cm}^{-1}$ , and the C—O band was shifted to 1040  $\text{cm}^{-1}$ .

### Reaction of THP and Its Adducts with Ammonia

A solution of THP (2.48 g, 0.02 mole) in 25 ml anhydrous ethanol, contained in a 50-ml flask fitted with a reflux condenser and a gas inlet tube extending

under the surface, was purged with nitrogen for 30 min and then treated with ammonia for 15 min. An exothermic reaction set in, and white solids separated all at once. After 5 min, the solids were collected on a filter, rinsed with ethanol, and dried overnight in a vacuum desiccator, leaving 1.24 g (59%) of hard, white solid insoluble in water or any of the common organic solvents. A sample was dried in a drying pistol at 80°/1 mm for analysis (Table I). The N:O:P ratio was 0.75:1.25:1, indicating 75% conversion of the THP to structure III. IR (KBr): 3300 *vs* (O—H), 2780 *s*, 1650 *m* (N—H), 1400 *s*, 1240 *m*, 1140 *s*, 1065 *s*, 1010 *vs* (C—O), and 875 *m*, *br*  $\text{cm}^{-1}$ . The presence of the 1650  $\text{cm}^{-1}$  N—H deformation band was evidence that the product was not crosslinked like Kasem's product.<sup>12</sup>

A similar reaction with water as the solvent produced some heat owing to solution of the ammonia, but no solids separated until the next day. The product, triturated under water, filtered, and dried, gave an infrared spectrum similar to the above, but with an even stronger N—H deformation band. The N:O:P ratio, based on the analyses (Table I), was 1:1.25:1.

The THP/aldehyde adducts Ib and II, dissolved in a small amount of water and treated with ammonia, both deposited white solids immediately. Purging with nitrogen was unnecessary. The products, triturated under water, filtered, and dried, gave infrared spectra similar to those described above. The N:O:P ratios, based on the analyses (Table I), were 0.9:1:1.4 for the acetaldehyde and 1:1:1 for the butyraldehyde product, the latter providing the best fit to the proposed structure (III).

A solution of THP (2.48 g, 0.02 mole) and chloral (3.31 g, 0.02 mole) in 10 ml water was purged with nitrogen, exposed briefly to ammonia (5 min), purged again, and filtered. The product was triturated under water, filtered, and dried, giving 2.03 g (70.5%) of pale yellow solid. IR (KBr): 3400 *vs* (O—H), 3250 *s*, 2900 *m*, 2800 *m*, 1640 *m* (N—H), 1420 *m*, 1250 *m*, 1140 *m*, 1075 *s*, 1020 *m* (C—O), 875 *m*, *br*, 820 *m* (C—Cl), and 794 *m*  $\text{cm}^{-1}$ .

ANAL. Calcd. for  $\text{C}_{10}\text{H}_{23}\text{Cl}_3\text{N}_3\text{O}_3\text{P}_3$ : C, 27.76; H, 5.36; Cl, 24.59; N, 9.72; P, 21.48. Found: C, 27.83; H, 5.17; Cl, 23.40; N, 9.02; P, 20.64.

A 0.7725 g portion of this product was hydrolyzed with 25 ml of 1N sodium hydroxide for 1 hr at 60–70°, filtered, rinsed with water and dried, giving 0.4892 g (71.9%) of pale yellow solid. IR (KBr): 3400 *vs* (O—H), 3250 *s*, 2900 *m*, 2800 *m*, 1650 *m* (N—H), 1420 *m*, 1250 *m*, 1145 *vs*, 1035 *s* (C—O), and 865 *m*, *br*  $\text{cm}^{-1}$ .

ANAL. Calcd. for  $\text{C}_{10}\text{H}_{23}\text{N}_3\text{NaO}_5\text{P}_3$ : C, 31.50; H, 6.08; Cl, none; N, 11.03; P, 24.37. Found: C, 31.80; H, 6.34; Cl, 0.23; N, 10.84; P, 24.78.

### Reaction of Ib with Dimethylamine

A solution of Ib (8.40 g, 0.05 mole) in 15 ml water, contained in a 50-ml flask fitted with a reflux condenser and a gas inlet tube extending under the surface, was purged for 30 min with nitrogen, followed by dimethylamine. Ice cooling was applied as necessary. When the flask was full, the addition was stopped and the contents were stripped on a rotary evaporator. The residue (9.05 g) was distilled under nitrogen, giving 6.55 g (63.9%) tris(dimethylaminomethyl)-phosphine,  $b_{0.7}$  78°–82°,  $n_D^{25}$  1.4790; lit.<sup>13</sup>  $b_{0.9}$  78°–80°,  $n_D^{25}$  1.4795. The identity of the product was confirmed by comparison of its infrared spectrum with that of a sample,  $b_{0.4}$  65°–67°, prepared from Thpc.<sup>14</sup>

TABLE I  
Analysis of Polymers Prepared from THP, Ib, or II, and Gaseous Ammonia

Reagent	Solvent	%C	%H	%N	%P
THP	H <sub>2</sub> O	35.92	6.98	12.19	27.27
THP	EtOH	34.95	7.26	9.95	29.19
THP, acetaldehyde (Ib)	H <sub>2</sub> O	35.75	6.92	10.73	27.17
THP, butyraldehyde (II)	H <sub>2</sub> O	34.95	7.16	13.44	29.62
Calcd for C <sub>3</sub> H <sub>8</sub> NOP (III)		34.29	7.67	13.33	29.48

TABLE II  
Effect of Aldehydes on the THP/Ammonia Fabric Treatment

Aldehyde	Undried		Dried 3 min at 85°	Dried 10 min at 85°	Air dried
	% Add-on	O.I.	% Add-on	% Add-on	% Add-on
None					
Conventional	7.6		5.1	0.9	
Rapid quench	0.8		0.8	0	5.3
Delayed quench	1.7				7.5
Formaldehyde					
Rapid quench	14.4	0.327	8.9	0.9	9.5
Delayed quench	15.2	0.321			12.1
Acetaldehyde					
Conventional	12.0	0.319	9.6	1.0	
Rapid quench	3.5		1.8	1.8	5.0
Delayed quench	9.6	0.280			7.6
Butyraldehyde					
Conventional	12.1	0.328	4.1	0.8	
Rapid quench	1.8		0.8	0.8	6.1
Delayed quench	8.4	0.280			13.3
Galactose					
Rapid quench	0		0.9	0	0
Delayed quench	1.6				2.5
Chloral					
Rapid quench	16.0	0.330	9.7	6.2	11.9
Delayed quench	17.0	0.345			18.5
Glyoxal					
Rapid quench	1.7		0.9	1.3	

### Fabric Treatments

The fabric used in this work was an 8-oz olive-drab cotton sateen, having an oxygen index<sup>1b</sup> value of 0.198.

In a typical experiment, a 6 × 12 in. fabric swatch was padded, 2 dips and 2 nips, through 50.0 g of solution containing 14.4 g (0.10 mole) 87% THP, 14.7 g (0.1 mole) 30% acetaldehyde, and 0.5 g of a wetting agent (Triton X-100), dried 3 min at 80° in a forced-draft oven, exposed to ammonia for 10 min in an enclosed chamber at room temperature, rinsed 30 min in hot, running tap water, and allowed to air dry. The wet pickup was 63% and the add-on, 9.6% (Table II, column 2).

Variables studied in this work were the aldehyde, the drying time, and the quenching procedure. The data are summarized in Table II.

### Analyses

Analysis for phosphorus and chlorine in fabric samples was by x-ray fluorescence,<sup>15</sup> and nitrogen by the Kjeldahl method, after digestion with sulfuric acid. Polymer samples were analyzed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer 137B instrument with NaCl optics. Measurements of pH were made with a Beckman Zeromatic pH meter equipped with a combination electrode.

## RESULTS AND DISCUSSION

### Reaction of THP with Aldehydes

When formalin is added to a tertiary phosphine such as triethylphosphine,<sup>16,17</sup> tributylphosphine,<sup>18</sup> or tris(hydroxymethyl)phosphine,<sup>19</sup> the solution becomes alkaline due to formation of the quaternary phosphonium hydroxide:



where R = Et, Bu, or CH<sub>2</sub>OH). The pH of a 0.5M THP solution, initially 6.4, rose steadily upon the dropwise addition of 37% formalin solution, reaching 7.4 at the equivalence point and leveling off at 7.9 after a large excess of formalin had been added. Under the same conditions, acetaldehyde (30%) raised the final pH to 7.0, chloral (30%) to 7.2, and glyoxal (40%) to 7.3. The pH of the chloral and glyoxal solutions gradually reverted to 6.5 on standing.\*

THP was shaken with full-strength acetaldehyde and allowed to evaporate at room temperature overnight, giving a product having a 2:1 ratio of acetaldehyde to THP. Pumping down in a vacuum desiccator reduced the ratio to 1:1. Both products showed strong O—H absorption and very weak C=O absorption in the infrared. They were evidently the phosphonium hydroxide Ib and its hemiacetal Ia, as shown below:



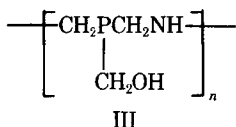
Butyraldehyde, heated at reflux with THP and then stripped of excess aldehyde under vacuum at 70°, gave the hemiacetal II, corresponding to Ia.

Upon exposure of Ib or II to gaseous ammonia, a strongly exothermic reaction ensued, and white solids separated within a few minutes. The reaction was faster when the Ib or II was dissolved in a small amount of water before exposure to gaseous ammonia, but no solids separated when the solution was treated with ammonium hydroxide.

THP itself developed neither exotherm nor solids upon exposure to gaseous ammonia, whether or not the THP was dissolved in water, although, after standing overnight, solids separated in both cases. With ethanol as the solvent, an exothermic reaction set in after 15 min, depositing a mass of white solids. These reactions were quite slow compared with the reaction of ammonia with Ib, II, or THPOH.

\* With full-strength THP and equimolar quantities of the aldehydes, Reuter et al. reported a rise to pH 8.5 with 30% formalin or 10% glyoxal, and to "weakly alkaline" with 30% acetaldehyde.<sup>19</sup> Vullo's observation that THP produced no increase in pH when added to neutral formalin<sup>18</sup> was based on an experiment with an indicator, phenolphthalein, that is not sensitive to pH in this region.

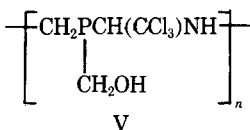
Elemental analyses on the polymers formed in these reactions (Table I) suggest that all four products have the same composition, approaching the empirical formula  $C_3H_8NOP$ . The variation in nitrogen content from one product to another reflects the extent of completion of the reaction. The best fit to this empirical formula is a linear polymer (III) containing a single phosphorus, nitrogen, and oxygen atom in each repeating unit\*:



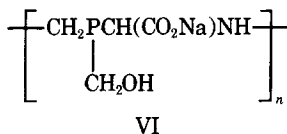
This structure is supported by the infrared spectra, which all show strong, broad absorption in the O—H (and N—H) regions, and strong absorption in the  $1010\text{ cm}^{-1}$  region characteristic of C—O stretching in tertiary methylol phosphines. The C—O stretching band appears at  $1010\text{ cm}^{-1}$  in THP, at  $1040\text{--}1050\text{ cm}^{-1}$  in THPO and Thpc<sup>20</sup> and at  $1025\text{--}1035\text{ cm}^{-1}$  in THP·HgX<sub>2</sub> complexes.<sup>9</sup> A shift to higher wavelengths also appears in the IR spectra of the substituted tertiary phosphines  $\text{RP}(\text{CH}_2\text{OH})_2$ .<sup>9</sup>

An experiment in which Ib was treated with dimethylamine gas instead of ammonia gave a 63.9% yield of tris(dimethylaminomethyl)phosphine,  $(\text{Me}_2\text{NCH}_2)_3\text{P}$ , identical to the product obtained from Thpc.<sup>13</sup> If the acetaldehyde had remained and formaldehyde had been released, the product would have been a mixed tertiary phosphine. Clearly, the aldehydes used in the preparation of the quaternary phosphonium hydroxides Ib or II were not present in the amino products, whether monomeric or polymeric.

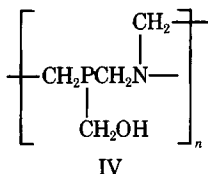
In contrast, exposure of THP to ammonia in the presence of chloral gave a pale-yellow polymer whose composition approached the empirical formula  $C_{10}H_{23}Cl_3N_3O_3P_3$ , suggesting a 2:1 copolymer of III and V:



Hydrolysis of this product with 1*N* sodium hydroxide removed the chlorine, giving a 2:1 copolymer of III and VI:



\* The THP/ammonia polymer prepared by Kasem et al.<sup>12</sup> also had a 1:1:1 ratio, but its carbon content was high. We ascribe this to formaldehyde crosslinking of the nitrogens on adjacent polymer chains, resulting in a structure IV:



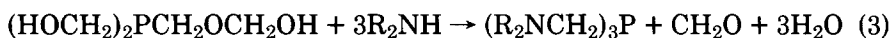
The absence of N—H absorption in the infrared provides support for this structure.

Consideration of possible mechanisms should provide some insight into the nature of this reaction.

A direct reaction between THP and an amine, shown in eq. (2), probably occurs only when no aldehyde is present. The reaction of formaldehyde-free THP with primary amines such as aniline<sup>14</sup> and with secondary amines such as morpholine<sup>21</sup> or diphenylamine<sup>22</sup> follows this course:



When an aldehyde is present, the reaction can take two paths, depending on which reagent the aldehyde reacts with first. If it reacts with the THP, a reactive intermediate is formed which then reacts with the amine, displacing formaldehyde, eq. (3). The reactive intermediate could be a P-methylol derivative such as the zwitterion<sup>22</sup>  $(\text{HOCH}_2)_3\text{P}^+\text{CH}_2\text{O}^-$ , or an O-methylol derivative such as THP hemiformal.<sup>21</sup> The evidence favors the O-methylol derivative (see Appendix):

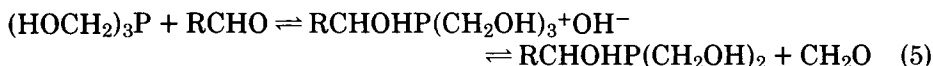


If the aldehyde first reacts with the amine, a reactive intermediate such as  $\text{R}_2\text{NCH}_2\text{OH}$  or  $\text{CH}_2(\text{NR}_2)_2$  is formed, which then reacts with the THP to displace formaldehyde, eq. (4):



Either mechanism explains the strongly catalytic effect of formaldehyde on the reactions of THP with primary amines such as hexamethylenediamine<sup>8</sup> and with secondary amines such as diphenylamine.<sup>22,23</sup> We favor the third mechanism because it more closely resembles that of the Mannich reaction, where the reaction of the aldehyde with the amine has been found to precede the reaction with the active hydrogen compound.<sup>24</sup>

In the third mechanism, the aldehyde that reacts with the amine should be retained in the product. However, the aldehyde exchange process shown in eq. (5) enables the amine to react with any aldehyde (or hemiacetal) present in the system:



Under these circumstances, the amine can (and did) react with the aldehyde bearing the most electron-deficient carbonyl carbon, i.e., formaldehyde in preference to acetaldehyde or butyraldehyde, and chloral in preference to formaldehyde. In practice, the reaction with chloral gave a mixed product, the competition between the aldehydes favoring formaldehyde by 2:1. No doubt, other factors such as steric hindrance or rate of reaction influenced the outcome in this case.

The question of why the reaction stopped at the disubstitution stage (III) when the amine was ammonia remains. We suggest that this reflects the change in state from monomer to polymer, removing the reactants physically from the reaction medium. Polymer III, though less reactive, should still be capable of reacting with formaldehyde, introducing methylene crosslinks without altering the N:O:P ratio, or with ammonia, changing the N:O:P ratio ultimately to 2:0:1.

Fabrics treated with the THPOH/ammonia finish have N:P ratios ranging from 0.75:1 to 1.25:1, depending on the fabric construction,<sup>2,3</sup> the base used to neutralize the Thpc,<sup>6</sup> and other variables. The presence of oxygen in these finishes before oxidation has not been recognized heretofore.

### Fabric Treatments

During these experiments, it was discovered that the THP/ammonia polymer could be prepared by mixing equimolar quantities of THP and an aldehyde (formaldehyde, acetaldehyde, butyraldehyde, chloral, etc., but not glyoxal) in water and exposing the solution to gaseous ammonia without isolating the adduct. This technique was adopted for the fabric treatments listed in Table II.

As in the THPOH/ammonia process, the conventional ammonia treatments gave add-ons highly sensitive to drying, falling off rapidly as the moisture content of the padded fabrics decreased.<sup>3</sup> The best results were obtained when the fabrics were cured in the damp state, fresh from the squeeze rolls (column 1). Those which had a 12% add-on appeared to be flameproofed, passing the match test<sup>1a</sup> at an angle of 135° and the oxygen index test<sup>1b</sup> at O.I. values well above 0.26.

To heighten the difference between the aldehydes, the procedure was modified by reducing the ammonia exposure time to 5 min and quenching the fabrics in hot running tap water as soon as they were removed from the ammonia chamber. The immediate quench favored those aldehydes that induced the most rapid polymer formation. Acetaldehyde produced a low add-on, butyraldehyde and glyoxal very little add-on, and galactose no add-on at all. The only aldehydes that showed up well in this experiment were formaldehyde and chloral. Fabric swatches treated with these aldehydes had O.I. values near 0.33, and could not be ignited with a match, even when suspended vertically. As in the conventional treatment, the add-ons fell off as the moisture content of the padded fabrics decreased, all but chloral becoming negligible at the 10-min point (column 3). When the padded fabrics were suspended in the hood for 4 hr and allowed to air dry before exposure to ammonia, all but galactose (including the control) had moderate to good add-ons (column 4).

Since the test appeared to be too severe, the procedure was modified by suspending the test fabrics in the hood *after* the ammonia exposure and allowing them to equilibrate in air before quenching. Acetaldehyde and butyraldehyde showed up somewhat better than in the rapid quench treatment, but only chloral consistently produced add-ons comparable to formaldehyde.

Analyses on the formaldehyde- and chloral-treated fabrics are given in Table III. The N:P atomic ratio varied from 0.70 to 0.96 for the formaldehyde-treated fabrics, and 0.81 to 0.95 for the chloral-treated fabrics. The latter also contained low levels of chlorine, varying in Cl:P atomic ratio from 0.11 to 0.20. Soap-soda boiling<sup>6</sup> stripped the chlorine from the fabric.

### CONCLUSIONS

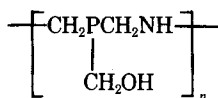
THP reacts with aldehydes in aqueous solution, forming 1:1 and 1:2 adducts formulated as O-adducts (hemiacetals), together with sufficient P-adduct (phosphonium hydroxide) to account for the increase in basicity. The adducts



TABLE III  
Analyses of Selected Treated Fabrics

Aldehyde	Undried		Dried 3 min at 85°		Dried 10 min at 85°		Air dried	
	%P	%N	%P	%N	%P	%N	%P	%N
Formaldehyde								
Rapid quench	3.82	1.63	3.48	1.27	0.25	0.08	3.44	1.09
Delayed quench	3.72	1.61					3.39	1.18
Chloral								
Rapid quench	3.97 (Cl, 0.60)	1.48	2.81 (Cl, 0.45)	1.03	2.09 (Cl, 0.48)	0.83	3.43 (Cl, 0.70)	1.27
Delayed quench	3.70 (Cl, 0.47)	1.59					3.81 (Cl, 0.74)	1.45

react rapidly with ammonia, forming polymers having a single phosphorus, nitrogen, and oxygen atom in each repeating unit. Similar polymers are obtained with mixtures of THP and the aldehydes and (more slowly) with THP alone. Aldehydes such as acetaldehyde or butyraldehyde, which are less nucleophilic than formaldehyde, are not incorporated in the polymers. These, therefore, have the common structure



Chloral, more nucleophilic than formaldehyde, is incorporated to some extent, but the chlorine is sensitive to base.

When applied to cotton sateen by the conventional THPOH/ammonia process, the THP/aldehyde adducts or mixtures produce flameproofed fabrics. Rapid quenching after ammoniation favors those aldehydes that induce the most rapid polymer formation. Under these conditions, only chloral produces results comparable to formaldehyde, but soap-soda boiling strips the chlorine from the fabric.

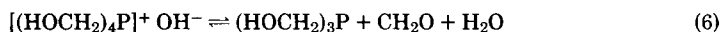
The structure of THPOH is discussed in the Appendix.

## Appendix

### The Structure of THPOH

This discussion is presented in an effort to dispel some of the confusion concerning the structure of THPOH. It is our thesis that the properties of THPOH are adequately explained in terms of the equilibrium expression comprising THPOH, THP, formaldehyde, and water, eq. (6), and that the acronym THPOH should be retained because it uniquely describes this reagent.

The acronym was first used in 1963 by Filipescu et al.<sup>25</sup> to describe the product obtained when Thpc is neutralized with lead carbonate or sodium hydroxide, though earlier references to the compound tetrakis(hydroxymethyl)phosphonium hydroxide exist.<sup>19,26-30</sup> Filipescu stated that "the THPOH (tetrakis(hydroxymethyl)phosphonium hydroxide) is believed to exist in equilibrium with tris(hydroxymethyl)phosphine (THP), i.e.,



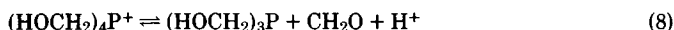
It was in this sense that the acronym was used in our original papers on the THPOH/ammonia finish.<sup>2,3</sup>

The existence of THPOH as a discrete compound was challenged by Vullo on the grounds that no new phosphonium peak appeared in the  $^{31}\text{P}$  nuclear magnetic resonance spectrum of THPOH solution, whether prepared by neutralizing Thpc or by dissolving THP in formalin. New peaks appearing in the tertiary phosphine region near THP were ascribed to the mono-, di-, and trihemiformals of THP.<sup>18</sup>

Titration of Thpc with sodium hydroxide produces a curve with a pH of about 8.8 at the equivalence point, characteristic of a weak acid. Calculation of the acid dissociation constant for the equilibrium



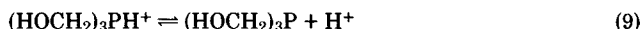
gives  $\text{p}K_a$  values that are not constant, increasing steadily<sup>31</sup> from 4.41 to 5.07. If, however, the zwitterion dissociates further to THP and formaldehyde, the equilibrium changes to the following:



The  $\text{p}K_a$  values must be corrected at each point for the formaldehyde concentration, either by subtracting<sup>31</sup>  $\log [\text{CH}_2\text{O}]$  from the  $\text{p}K_a$  or by squaring the THP concentration, since the concentrations of THP and  $\text{CH}_2\text{O}$  are equal. The overall dissociation constant, which Fodor called  $\text{p}K_d$ , is now truly constant<sup>31</sup> at  $7.06 \pm 0.01$ .

This argument, coupled with the absence of a suitable peak in the  $^{31}\text{P}$  NMR spectrum, eliminates the zwitterion of eq. (7) as a stable component of THPOH solutions (though not, as often invoked,<sup>11,21,31,32</sup> as a transient intermediate).

THP itself is a much weaker base.\* Fodor<sup>31</sup> estimated the  $\text{p}K_a$  for the equilibrium



to be less than 3. Based on displacement experiments, we found THP to be a stronger base than triphenylphosphine ( $\text{p}K_a$  2.30), but not as strong as tributylphosphine ( $\text{p}K_a$  8.43).<sup>9</sup> The theoretical  $\text{p}K_a$ , calculated<sup>9</sup> by means of the Taft substituent constant for the hydroxymethyl group, is 3.40.

Clearly, the properties of THPOH solutions are not adequately described by THP, even though the latter may be the major component of the solution. The evidence favors the equilibrium of eq. (6), wherein THP and formaldehyde (or THP hemiformal) are the major components and the phosphonium hydroxide is present in an amount just sufficient to give the solution its feebly basic properties. The concentration of the phosphonium hydroxide is, of course, far too small to be detected by  $^{31}\text{P}$  NMR. A parallel can be drawn with ammonium hydroxide, wherein a minute quantity of  $\text{NH}_4^+\text{OH}^-$ , formed by hydrolysis of ammonia, accounts for the alkalinity of ammonia solution, even though the latter consists almost entirely of unionized hydrated ammonia.<sup>34</sup>

The extent of hemiformal formation varies with the solvent, amounting to 37% in water, but only 5% in methanol.<sup>18</sup> This is not surprising, since formaldehyde exhibits a greater affinity for alcohols than for water. Hemiacetal formation reflects the extent to which THP, as an alcohol, can compete with the solvent for the excess aldehyde.

The equilibrium of eq. (6) provides a mechanism for the rapid exchange of aldehyde groups. The importance of this aspect has been discussed in the text.

Another consequence of the equilibrium is that the pH of neutral THPOH solutions is concentration dependent. The pH of a 0.01M solution is 8.53 and increases by one pH unit for each tenfold increase in concentration. In practical terms, the 40% THPOH solution commonly used as a textile finishing reagent should have a pH of about 11. Obviously, the reagent would decompose before this point was reached.

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## References

1. W. A. Reeves and G. L. Drake, Jr., *Flame Resistant Cotton*, Merrow, Watford, Herts., England, 1971; (a) pp. 14–16; (b) pp. 19–21; (c) pp. 33–52.

\* The  $\text{p}K_a$  value of 5.5 reported by Grayson<sup>32</sup> was determined by titration of Thpc, and does not, therefore, apply to formaldehyde-free THP. Lucken<sup>33</sup> reported the same value for THP without disclosing how it was obtained.

2. J. V. Beninate, E. K. Boylston, G. L. Drake, Jr., and W. A. Reeves, *Am. Dyest. Rep.*, **57**, 981 (1968).
3. J. V. Beninate, E. K. Boylston, G. L. Drake, Jr., and W. A. Reeves, *Text. Ind.*, **131**(11), 110 (1967).
4. R. J. Berni, D. M. Soignet, J. V. Beninate, and M. W. Pilkington, *Text. Res. J.*, **42**, 576 (1972).
5. T. A. Calamari, S. P. Schreiber, and W. A. Reeves, *Text. Chem. Color.*, **7**, 65 (1975).
6. A. W. Frank and G. L. Drake, Jr., *Text. Res. J.*, **44**, 292 (1974).
7. G. M. Wagner, P. E. Hoch, and I. Gordon (to Hooker Chemical Corp.), U.S. Pat. 3,146,212 (1964); *Chem. Abstr.*, **62**, 4159e (1965).
8. D. J. Daigle and D. J. Donaldson, *J. Appl. Polym. Sci.*, **14**, 248 (1970).
9. A. W. Frank and G. L. Drake, Jr., *J. Org. Chem.*, **36**, 549 (1971).
10. M. Reuter and L. Orthner (to Farbwerke Hoechst A.-G.) U.S. Pat. 3,030,421 (1962).
11. A. W. Frank and G. L. Drake, Jr., *Text. Res. J.*, **43**, 633 (1973).
12. M. A. Kasem, H. R. Richards, and C. C. Walker, *J. Appl. Polym. Sci.*, **15**, 2237 (1971).
13. H. Coates and P. A. T. Hoye (to Albright & Wilson (Mfg.) Ltd.), Ger. Pat. 1,077,214 (1960).
14. A. W. Frank and G. L. Drake, Jr., *J. Org. Chem.*, **37**, 2752 (1972).
15. V. W. Tripp, B. Piccolo, D. Mitcham, and R. T. O'Connor, *Text. Res. J.*, **34**, 773 (1964).
16. J. N. Collie, *J. Chem. Soc.*, **127**, 964 (1925).
17. K. A. Petrov, A. I. Gavrilova, V. M. Nam, and V. P. Chuchkanova, *Zh. Obshch. Khim.*, **32**, 3711 (1962); *Chem. Abstr.*, **58**, 12594h (1963).
18. W. J. Vullo, *J. Org. Chem.*, **33**, 3665 (1968).
19. M. Reuter, L. Orthner, F. Jakob, and E. Wolf (to Farbwerke Hoechst A.-G.) U.S. Pat. 2,937,207 (1960); *Chem. Abstr.*, **54**, 22362a (1960).
20. M. Anteunis, M. Verzele, and G. Dacremont, *Bull. Soc. Chim. Belges*, **74**, 622 (1965).
21. S. E. Ellzey, Jr., W. J. Connick, Jr., G. J. Boudreaux, and H. Klapper, *J. Org. Chem.*, **37**, 3453 (1972).
22. D. J. Daigle, A. B. Pepperman, and W. A. Reeves, *Text. Res. J.*, **41**, 944 (1971).
23. D. J. Daigle, W. A. Reeves, and D. J. Donaldson, *Text. Res. J.*, **40**, 580 (1970).
24. B. B. Thompson, *J. Pharm. Sci.*, **57**, 715 (1968).
25. N. Filipescu, L. M. Kindley, H. E. Podall, and F. A. Serafin, *Can. J. Chem.*, **41**, 821 (1963).
26. Soc. Anon. Manufactures Glaces Produits Chimiques Saint-Gobain, Chauny & Cirey, *Fr. Pat.* 1,011,978 (1952); *Chem. Abstr.*, **51**, 14785g (1957).
27. M. Reuter and L. Orthner (to Farbwerke Hoechst A.-G.) Ger. Pat. 1,041,957 (1958); *Chem. Abstr.*, **55**, 1444b (1961).
28. M. Reuter (to Farbwerke Hoechst A.-G.) Ger. Pat. 1,064,061 (1959); *Chem. Abstr.*, **55**, 11301h (1961).
29. Kh. R. Raver, A. B. Bruker, and L. Z. Soborovskii, *Zh. Obshch. Khim.*, **32**, 588 (1962); *Chem. Abstr.*, **58**, 6857c (1963).
30. Kh. R. Raver, L. Z. Soborovskii, and A. B. Bruker, USSR Pat. 143,395 (1962); *Chem. Abstr.*, **57**, 9882i (1962).
31. L. M. Fodor, A Study of Some Oxidation Reactions of the Tetrakis-hydroxymethyl Phosphonium Cation, Ph.D. Dissertation, Cornell University, Ithaca, N. Y., 1963.
32. M. Grayson, *J. Am. Chem. Soc.*, **85**, 79 (1963).
33. E. A. C. Lucken, *J. Chem. Soc.*, A 1357 (1966).
34. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 2nd ed., Wiley-Interscience, New York, 1966, p. 333.