Formaldehyde: The Key to Polymerization Between THPOH and NH_4OH

The chemical nature of the solution resulting from the neutralization of tetrakis-(hydroxymethyl)phosphonium chloride (THPC) with a base has been the subject of much interest in recent years. THPC is used commercially in the production of flame-resistant cellulosic textiles. A majority of the authors[1-6] have written the neutralization reaction of THPC as

$$(HOCH_2)_4\overset{\oplus}{P}Cl + NaOH \rightarrow NaCl + H\overset{O}{\overset{\|}{C}}H + H_2O + (HOCH_2)_3P(THP).$$

French workers[7] and Filipescu et al.[8] proposed an equilibrium between THP and tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH).

Vullo,[9] more recently, studied the neutralization of THPC by ^{31}P nuclear magnetic resonance spectroscopy. He found that three species were in the solution: tris-(hydroxymethyl)phosphine oxide (THPO) and two phosphines. One was THP and the other, a hemiacetal resulting from the reaction of THP with the byproduct formaldehyde:

$$(HOCH_2)_3P + H\overset{O}{\overset{\|}{C}}H \leftrightharpoons HOCH_2OCH_2{-}P(CH_2OH)_2.$$

Textile workers have neutralized THPC and referred to the solution as "THPOH," realizing that it is a mixture of products.[10] They have used the "THPOH" solution as the basis for a flame-resistant finish. As with THPC, "THPOH" solutions have been incorporated with amides and then with methylol derivatives. However, "THPOH" reacts immediately with ammonia and diamines to form insoluble polymers.

Other workers[11] found that copper salts inhibited the instantaneous polymerization of "THPOH" solutions with aqueous ammonium hydroxide. These workers believe from molar ratio studies that the phosphines in solution are complexed by the copper salts. The proposed complex being formed is felt to be between one copper ion and four trivalent phosphorus atoms. When the formulation was applied to cotton fabric, then heated to 130°–160°C, the complex was destroyed, allowing polymerization of ammonia and "THPOH" to take place in the cotton fibers.

To continue this work and prepare different polymers of THPOH, diamines such as 1,6-hexamethylenediamine were used in lieu of ammonia. However, it was found that copper salts do not inhibit the polymerization of "THPOH" solutions by the diamines. Vullo's work[4,9] showed that only one other compound, i.e., formaldehyde, is present in "THPOH" solutions in addition to the phosphines and THPO. A stable solution of "THPOH," diamine, and copper salt was then prepared by the addition of ammonium hydroxide. An equal molar ratio of ammonia to formaldehyde was needed for the stability of the solution because the formation of hexamethylenetetramine (hexamine) in the presence of excess formaldehyde or ammonia proceeds rapidly and essentially to completion according to the equation

$$6\ CH_2O + 4\ NH_3 \rightarrow (CH_2)_6N_4 + 6\ H_2O.$$

THP prepared by Gordon's procedure did not react at room temperature with the diamines to form a polymer immediately. However, a slow evolution of gas did take place. Also when a THP solution prepared by Gordon's procedure was mixed with ammonium hydroxide, no insoluble polymer was immediately produced. Instead, a gas which proved to be hydrogen slowly evolved:

$$(HOCH_2)_3P + \overset{\ominus}{O}H + H_2O \rightarrow (HOCH_2)_3P{=}O + H_2 + \overset{\ominus}{O}H$$

$$(HOCH_2)_3P + H_2O + BOH \rightarrow (HOCH_2)_2P(O)(OB) + CH_2O + 2H_2$$

In both cases, diamine or ammonia, a precipitate very slowly formed. When formaldehyde was added to a solution of THP and ammonia hydroxide, a polymer immediately formed. This new evidence indicates that the polymerization reaction of "THPOH" solution with amines or diamines must be initiated by formaldehyde or the hemiacetal.

When hexamine was added to a THP solution, precipitation took place within 3–8 hr dependent upon the pH of the solution. Although hexamine is stable in water at room temperature, its stability being increased by the addition of a weak base, it decreases slightly at higher temperatures and rapidly decreases with lower pH's:

$$(CH_2)_6N_4 + 4\ H^+ + 6\ H_2O \rightarrow 4\ \overset{\oplus}{NH_4} + 6\ CH_2O.$$

A solution of THP (13.3%) and concentrated ammonium hydroxide (33%) were padded onto cotton fabric to an 80% pickup and cured at temperatures of 140°, 150°, and 160° for 10 min. A solution of THP (15%) and hexamine (12.5%) was also padded and cured on cotton fabric in a like manner. After a water rinse, only the fabric treated with the solution containing THP and hexamine had an add-on (12%).

From the above reactions it is clear that THP does not react readily with amines unless formaldehyde is present. This preliminary investigation is being continued toward discovering the type of polymer formed and the mechanism by which it is formed.

References

1. L. M. Fodor, Ph.D. Thesis, Cornell University, Ithaca, New York, 1963.
2. H. Hellman and O. Schumacker, *Angew. Chem.*, **72**, 211 (1960).
3. K. A. Petrov, V. A. Parshina, and M. B. Zuryanova, *J. Gen. Chem. U.S.S.R.*, **32**, 553 (1962).
4. W. J. Vullo, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 344 (1966).
5. M. Grayson, *J. Amer. Chem. Soc.*, **85**, 79 (1963).
6. I. Gordon and G. M. Wagner, U. S. Pat. 3,257,460 (1966).
7. French Pat. 1,011,978 (1952).
8. N. Filipescu, L. M. Kindley, H. E. Podall, and F. A. Serafin, *Can. J. Chem.*, **41**, 821 (1963).
9. W. J. Vullo, *J. Org. Chem.*, **33**, 3665 (1968).
10. J. V. Beninate, E. K. Boylston, G. L. Drake, Jr., and W. A. Reeves, *Text. Ind.*, **131**, 110 (1967).
11. D. J. Donaldson and D. J. Daigle, Textile Research Journal, **39**, No. 4, 363 (1969).

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Received July 31, 1969
Revised September 29, 1969