REVIEW

Commercial Synthesis of Monoalkyl Phosphates

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ABSTRACT: Historically, phosphate esters have been prepared by the reaction of alcohols with phosphoric anhydride or polyphosphoric acid. Recently, hybrid reagents have been developed. A review of the commercial production of long-chain monoalkyl phosphate esters is presented. The titled esters are the subject of increased interest, especially in low-irritation surfactant formulations.

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Phosphate esters represent specialty surfactants fitting a number of niche markets (1). Beginning in the late 1950s, they have found application as antistatic agents, emulsifiers, wetting agents, and hydrotropes. Recently, surfactant market needs have demanded materials possessing improved properties, especially low-irritation and mildness properties. Nature provides many examples of these types of products, one example being phospholipids. This observation suggests that phosphate esters are materials exhibiting mild, nonirritating properties. As a result, considerable effort recently has been aimed at developing methods for preparing highly pure monoalkyl phosphates. Because of their compatibility with skin and inherent low-irritation characteristics, these species find use in personal-care applications, such as skin cleansers, body washes, shampoos, and oral care formulations. Specifically, in skin irritation, skin roughness, and skin tightness tests, monoalkyl phosphates exhibited superior performance when compared to ether sulfates, sodium lauryl sulfate, soap and acyl L-glutamates (2). Although high-purity monoalkyl phosphates may be necessary for premium applications, examination of foaming and solubility properties as a function of composition shows that surfactant properties decrease markedly below a weight ratio of 70:30 monoalkyl to dialkyl phosphate but exhibit only a modest improvement above a 90:10 ratio (3). The classical method of synthesis, utilizing phosphoric anhydride, yields products containing large quantities of diester. Alternatively, use of polyphosphoric acid results in significant residual alcohol and high levels of phosphoric acid. The presence of phosphoric acid is undesirable because it forms salts on formulation, which can result in precipitation.

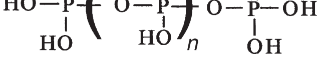
This review describes the commercial production of long-chain monoalkyl phosphates utilizing polyphosphoric acid, phosphoric anhydride, and their combinations.

POLYPHOSPHORIC ACID

Polyphosphoric acid (Scheme 1) consists of a mixture of linear, oligomeric chains of phosphorus and oxygen atoms (4).

The activity of polyphosphoric acid is expressed as percent phosphoric acid or percent P_2O_5. As the values of *n* and the corresponding percent phosphoric acid increase, the material becomes progressively more viscous. The oily liquid first becomes rubbery and finally a glassy solid (5). The linear structure of polyphosphoric acid makes it less reactive than the highly energetic tetrahedral phosphoric anhydride and usually requires heat to effect complete reaction.

Long-chain monoalkyl phosphates have traditionally been made *via* reaction of polyphosphoric acid with an alcohol or alcohol ethoxylate (6–9). Commercial polyphosphoric acid ranges in strength between 105 and 117%. The monoalkyl to dialkyl ratio increases with increasing reaction temperature and with decreasing strength of the polyphos-



$$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle HO}{|}}{P}}}\left(\mathrm{O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle HO}{|}}{P}}}\right)_n\mathrm{O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH}$$

SCHEME 1

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phoric acid (to a limit at pyrophosphoric acid) (10). Reaction of an alcohol with polyphosphoric acid results in cleavage of the polyphosphoric acid chain. Large amounts of orthophosphoric acid form because each chain produces, on average, one molecule of phosphoric acid. Reaction of the oligomeric chain with the alcohol species occurs principally at the terminus to form a phosphate ester and a molecule of phosphoric acid, exemplified in Equation 1,

$$\mathrm{ROH} + \mathrm{HO}\overset{\mathrm{O}}{\underset{\mathrm{OH}}{\mathrm{P}}}\mathrm{O}(\overset{\mathrm{O}}{\underset{\mathrm{OH}}{\mathrm{P}}}\mathrm{O})_n\mathrm{H} \longrightarrow n\ \mathrm{RO}\overset{\mathrm{O}}{\underset{\mathrm{OH}}{\mathrm{P}}}\mathrm{OH} + \mathrm{HO}\overset{\mathrm{O}}{\underset{\mathrm{OH}}{\mathrm{P}}}\mathrm{OH} \qquad [1]$$

The amount of phosphoric acid is equal to $1/n$ (see polyphosphoric acid structure) where n equals the average polymer chain length. Reaction of simple alcohols with 117% polyphosphoric acid is reported to produce 21.0 to 23.8 mol% phosphoric acid in good agreement with the 23.2 mol% predicted for 117% polyphosphoric acid (11). In commercial practice, an excess of polyphosphoric acid is employed to produce esters containing minimal quantities of residual alcohol (alcohol ethoxylate). However, for some applications a relatively high residual level of alcohol (ethoxylate) is desired; hence, an excess of alcohol is used. Niche products necessary to meet numerous application requirements have evolved with differing levels of nonionic alcohol or alcohol ethoxylate and phosphoric acid.

Typically (7,9), 0.3 to 1.5 moles of alcohol (alcohol ethoxylate) is reacted per mole of phosphorus pentoxide in 115% polyphosphoric acid at 50°C. The reaction mixture is heated to 105–110°C and held for 1–2 h. It is then cooled and packaged. The product is 70 to 90% monoester, 9 to 28% diester, and 0.1 to 12% nonionic (9).

Personal-care applications require minimal phosphoric acid and residual alcohol levels to minimize skin irritation and to provide ease of formulation (3). Furthermore, the presence of diester contributes a reduction in solubility, foam generation, and detergency properties.

To minimize these undesirable aspects, numerous approaches are described in the literature.

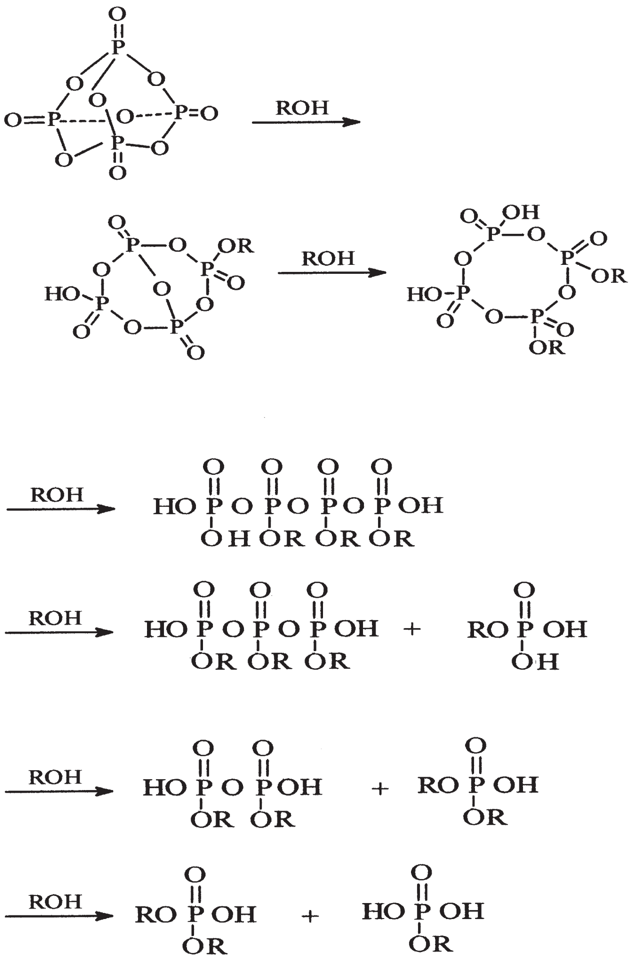
A novel extraction process (12–15) has been reported yielding 96 wt% of monoalkyl ester, only 2.3% phosphoric acid, and less than 1% each of dialkyl phosphate and residual alcohol. The process employs a fivefold excess of polyphosphoric acid, minimizing the level of unconverted alcohol. Because of the high viscosity generated, a solvent such as hexane is needed. Upon completion of the reaction, the mixture is extracted with aqueous isopropanol. The hexane layer containing the phosphate ester is extracted a second time with isopropanol. The hexane layer is then subjected to azeotropic distillation to remove any residual water and isopropanol. Next the phosphate ester is precipitated from the hexane. This batch process can be adapted to a continuous operation. Others (16,17) have less successfully tried to remove residual alcohol by steam distillation after partial neutralization.

PHOSPHORIC ANHYDRIDE

Traditionally, phosphate esters have been prepared by reaction of phosphoric anhydride with an alcohol or alcohol ethoxylate (18–21). At stoichiometric ratios, the reactants yield a mixture of mono- and dialkyl phosphates close to the theoretical 50:50 molar ratio. The overall reaction sequence is very complex, involving numerous intermediates, but it can be rationalized based on the tetrahedral structure of phosphoric anhydride (Scheme 2).

An alcohol molecule initially reacts with one of the phosphorus atoms of the tetrahedron, resulting in cleavage of an adjacent phosphorus oxygen bond and opening of the tetrahedron to a bicyclic intermediate. Successive reactions with alcohol lead to monocyclic and acyclic products.

In a typical process (19), alcohol (4–9 mol) is reacted with 1 mol P_4O_{10} under vigorous agitation so as to maintain the temperature of reaction under 50°C. The reaction is highly exothermic and requires cooling during phosphoric anhydride addition. The subsequent reactions are driven to



SCHEME 2

completion by heating to 100°C and holding for about 5 h. The result is a mixture of esters (Eq. 2)

$$P_4O_{10} + 6\ ROH \rightarrow 2(RO)_2P(O)OH + 2\ ROP(0)(OH)_2 \qquad [2]$$

The molar ratio can be manipulated between 65:35 and 35:65 by adjusting the alcohol and water proportions, i.e., by partially substituting water for alcohol in the reaction sequence (Eq. 3). The product distribution also differs depending on whether water is added before or after the alcohol (22,23).

$$\begin{aligned}(6 - n)\ ROH + nH_2O + P_4O_{10} &\rightarrow xH_3PO_4 \\ &+ y(RO)P(OH)(OH)_2 + z(RO)_2P(O)OH \qquad [3]\end{aligned}$$

where $x + y + z = 4$.

In practice, 100% monoalkyl phosphates cannot be made *via* this process. Water in a competitive reaction produces phosphoric acid.

HYBRID PROCESSES

Efforts to devise simpler processes, yielding long-chain monoalkyl phosphate compositions in the desirable performance ranges and eliminating the need for expensive purification and the attendant recycle steps, led to the development of modified or hybrid reagents.

Initially, a two-step process was developed (3,24) in which water was added to the phosphating agent. In the first step, the alcohol, phosphating agent, and water (or its equivalent in phosphoric or polyphosphoric acid, calculated as a composite of phosphoric anhydride and water) combine according to Equation 4:

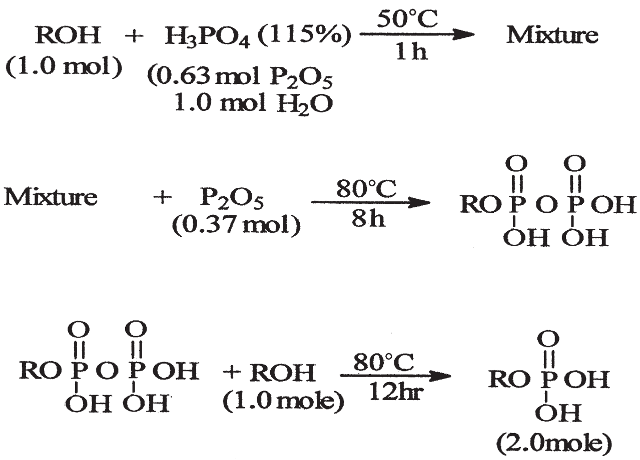
$$[C + B]/A = 1.2 \text{ to } 2.8 \qquad [4]$$

where A is moles of phosphating agent, expressed as P_2O_5, B is moles of water, including those present in the phosphating agent, and C represents moles of alcohol. Since P_2O_5 phosphating reagent requires three moles of alcohol plus water for a complete reaction, it is present in excess with the intent of preferentially forming the monoalkyl phosphate intermediate in the first step. After conversion of the more reactive phosphating reagent and intermediates to pyrophosphates, the remaining amount of alcohol, D, is added in a second step according to Equation 5:

$$[B + C + D]/A = 2.9 \text{ to } 3.1 \qquad [5]$$

This completes the conversion of the monoalkyl pyrophosphate intermediate to monoalkyl orthophosphates as illustrated in Scheme 3.

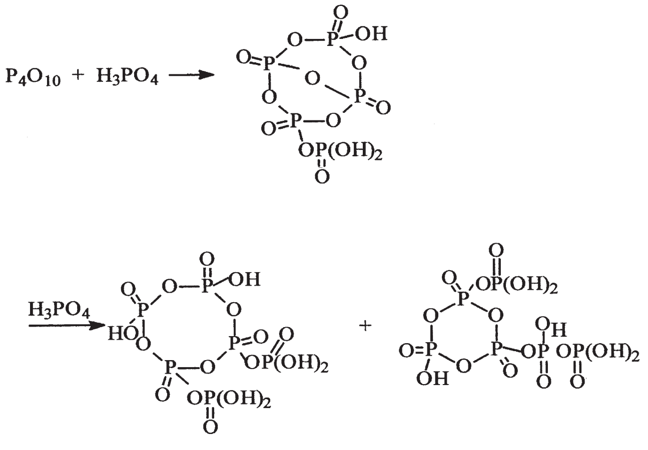
More recently, simpler processes have evolved based on phosphoric anhydride. A composite is prepared by blending phosphoric anhydride with phosphoric acid under moderate temperature (up to 60°C) (25–28). This can be envisioned as a reaction of the highly reactive tetrahedral bonds of phosphoric anhydride with phosphoric acid, producing monocyclic species of relatively short chains as intermediates. The hybrid reagent is not simply a mixture, but a discrete chemical reagent (28). Analysis by ^{31}P NMR spectroscopy indicates that 87 mol% of the phosphorus atoms exist as internal or cyclic groups with only a trace of phosphoric acid. Signals characteristic of phosphoric anhydride are absent.



SCHEME 3

Although the composite reagent consists of a range of intermediates, the average composition can be rationalized as being, at least initially, phosphate substituted tri- and tetrametaphosphoric acids (Scheme 4).

The reagent can be easily added to alcohol or alcohol ethoxylate, or it can be generated selectively in the reactant alcohol provided the temperatures are maintained so that the polyphosphoric acid and phosphoric anhydride do not react with alcohol but with each other. The reagent generates less heat upon reaction, resulting in less color and lower dioxane levels. Reagent strengths from 119 to 123% produce products with a mono- to dialkyl ratio above 80:20 with residual phosphoric acid and alcohol levels below 6%.



SCHEME 4

A typical process is as follows (26). To 7924 g lauryl alcohol (42.5 mol) are added 2265 g 115% polyphosphoric acid (26.5 mol) and 1129 g phosphoric anhydride (3.98 mol; 15.9 mol phosphorus) with rapid agitation and good cooling at maximum temperatures of 42 and 59°C during the respective addition periods. The alcohol-to-phosphorus ratio is 1.0. The mixture is heated to 85°C and held there for 11 h. The solution is then cooled to 65°C and can optionally be bleached with hydrogen peroxide to produce a clear colorless product. Analysis by NMR indicates a monoalkyl/dialkyl ratio of 84.5:14.5. The nonionic residue is 0.4%. The phosphoric acid content is 4.7%.

This simplification of the manufacturing criteria suggests that phosphate esters, historically small-volume products, are poised for penetration of larger-volume markets.

REFERENCES

1. Burnette, T.W., Nonionics as Surfactant Intermediates, in *Nonionic Surfactants,* edited by M.J. Schick, Marcel Dekker, New York, 1966, Vol. 1, p. 384.
2. Imokawa, G., Surfactant Mildness, in *Surfactants in Cosmetics*, 2nd edn., edited by M.M. Rieger and L.D. Rhein, Surfactant Science Series, Marcel Dekker, New York, 1997, Vol. 68, pp. 427–471.
3. Imokawa, G., H. Tsutsumi, T. Kurosaki, M. Hayashi, and J. Kakuse, U.S. Patent 4,139,485 (1979).
4. Thilo, V.E., and R. Sauer, Chemistry of the Condensed Phosphates and Arsenates XVII. The Course and Products of the Dehydration of Monophosphoric Acid H_3PO_4, *J. Prakt. Chem. 4*:324 (1957).
5. Boenig, I.A., M.M. Crutchfield, and C.W. Heitsch, Phosphoric Acid and Phosphates, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. edn., John Wiley & Sons, New York, 1982, Vol. 17, p. 518.
6. Woodstock, W.H., U.S. Patent 2,586,897 (1952).
7. Mansfield, R.C., U.S. Patent 3,235,627 (1966).
8. Mansfield, R.C., and J. Dupre, U.S. Patent 3,312,624 (1967).
9. Eisman, F.S., and L.M. Schenck, U.S. Patent 3,331,896 (1967).
10. Nelson, A., and A. Toy, The Preparation of Long-Chain Monoalkyl Phosphates from Pyrophosphoric Acid and Alcohols, *Inorg. Chem. 2*:775(1963).
11. Clark, F., and J. Lyons, The Alcoholysis of Polyphosphoric Acid, *J. Am. Chem. Soc. 88*:4401 (1966).
12. Kurosaki, T., J. Wakatsuki, H. Furugaki, and K. Kojima, U.S. Patent 4,670,575 (1987).
13. Aimono, K., T. Fujita, T. Funeno, and Y. Sasa, Jpn. Kokai 03 188,089 (1991).
14. Tsuyutani, S., K. Aimono, T. Funeno, and T. Fujita, Jpn. Kokai 05 148,276 (1993).
15. Takamura, K., and K. Aimono, Jpn. Kokai 05 271,255(1993).
16. Uphues, G., and J. Ploog, U.S. Patent 4,866,193 (1989).
17. Uphues, G., and J. Ploog, U.S. Patent 4,874,883 (1989).
18. Bertsch, H., U.S. Patent 1,900,973 (1933).
19. Nunn, L.G., Jr., and S.H. Hesse, U.S. Patent 3,004,056 (1961).
20. Nunn, L.G., Jr., U.S. Patent 3,004,057 (1961).
21. Lazarus, A.K., U.S. Patent 3,487,130 (1969).
22. Hochwalt, C.A., J.H. Lum, J.E. Malowan, and C.P. Dyer, Alkyl Esters of Phosphoric Acid, *Ind. Eng. Chem. 34*:20 (1942).
23. Kurosaki, T., J. Wakatsuki, T. Imamura, A. Matsunaga, H. Furugaki, and Y. Sasa, Monoalkylphosphate: Phosphation, Analysis and Properties, *Comun. Jorn. Com. Esp. Deterg. 19*:191 (1988).
24. Kurosaki, T., and A. Manba, U.S. Patent 4,350,645 (1982).
25. Reierson, R.L., U.S. Patent 5,554,781 (1996).
26. Reierson, R.L., U.S. Patent 5,550,274 (1996).
27. Reierson, R.L., U.S. Patent 5,463,101 (1995).
28. Reierson, R.L., U.S. Patent 6,136,221 (2000).

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