The Preparation of Long-Chain Monoalkyl Phosphates from Pyrophosphoric Acid and Alcohols

BY ARTHUR K. NELSON AND A. D. F. TOY

A new method for the preparation of long-chain monoalkyl phosphates, from crystalline pyrophosphoric acid and alcohols, is reported. Syntheses of monoalkyl phosphates containing eight, ten, twelve, and fourteen carbon atoms are described.

Commonly used methods for the preparation of monoalkyl phosphates involve the simultaneous formation of dialkyl phosphates.[1-5] At present, monoalkyl phosphates are available commercially only as components of such mixtures.[1] Separation of pure monoalkyl phosphates from such mixtures may be accomplished by ion-exchange techniques,[6] by distribution between solvents of differing polarity,[7] or by selective precipitation of a salt, usually of barium.[8] The choice of method depends upon the size and nature of the alkyl group. In many cases such separations are either tedious or difficult.

Methods reported in the literature for the preparation of monoalkyl phosphates include the permanganate oxidation of alkyl phosphites[9] or alkyl phosphonates[10] and the catalytic hydrogenolysis of diphenyl alkyl phosphates.[11] Long-chain monoalkyl phosphates with alkyl groups containing twelve, fourteen, sixteen, and eighteen carbon atoms were prepared by the latter method.

In view of the increasing use of various alkyl phosphates as selective metal extractants a relatively simple procedure for the preparation of monoalkyl phosphates would be desirable. We have found that long-chain monoalkyl phosphates may be prepared from crystalline pyrophosphoric acid and alcohols in accordance with the equation

$$H_4P_2O_7 + ROH = RH_2PO_4 + H_3PO_4 \qquad (1)$$
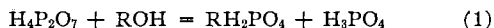
where R represents an alkyl group. Compounds prepared included mono-2-ethylhexyl phosphate, a liquid, and mono-n-decyl phosphate, mono-n-dodecyl phosphate, and mono-n-tetradecyl phosphate, all of which are white crystalline solids. The increased water solubility of short-chain monoalkyl phosphates limits the efficacy of the procedure for the separation of the reaction products which depends upon the extraction of the co-product orthophosphoric acid with water

from an organic solvent containing the monoalkyl phosphate.

The reactants were either mixed in an equimolar ratio or a slight excess of the acid was used. For the preparation of liquid monoalkyl phosphates use of a solvent is optional while for solid products an inert solvent, such as benzene, is necessary. All preparations were carried out at room temperature. Higher temperatures are unnecessary and deleterious. In the preparation of mono-2-ethylhexyl phosphate, at 50° a pronounced discoloration plus a small degree of dehydration of the alcohol to an alkene occurred. At 90°, alkene formation was dominant. Furthermore, pyrophosphoric acid melts incongruently at 54°. Melting of pyrophosphoric acid prior to dissolution and reaction would provide both orthophosphoric and triphosphoric acids in the liquid phase.

With vigorous stirring at room temperature pyrophosphoric acid was dissolved in the liquid phase within a few hours and the reactions, in this chain-length range, found to be about 80% complete in 24 to 36 hr. The extent of reaction may be determined at any time by a titrimetric procedure described in the Experimental section. Since it is not practicable to await completion of the reaction, which probably is second order, it is necessary to separate the product from unreacted alcohol and pyrophosphoric acid, in addition to the co-product, orthophosphoric acid. After dissolution of the reaction solution in ether and one or two aqueous extractions to remove inorganic acids, the monoalkyl phosphate was extracted into an aqueous solution at pH 12 by conversion to the water-soluble monoalkyl disodium phosphate, allowing recovery of unreacted alcohol from its ether solution. The pH of the aqueous phase then was adjusted to about 0.5 with hydrochloric acid. During this acidification the precipitation and dissolution of both the monosodium salt $RNaHPO_4$ and the so-called hemisodium salt $RNaHPO_4 \cdot RH_2PO_4$ may be observed. At pH 0.5 the monoalkyl phosphate was recovered by extraction into ether. Solid products were recrystallized from hexane. Both organic phosphates and orthophosphoric acid were effectively removed by one recrystallization. Purity was demonstrated by means of paper chromatography, titration, and attainment of a sharp melting point.

Small amounts of by-products such as monoalkyl pyrophosphates, dialkyl pyrophosphates, and dialkyl

(1) C. A. Hochwalt, J. H. Lum, J. E. Malowan, and C. P. Dwyer, *Ind. Eng. Chem.*, **34**, 20 (1942).
(2) E. Cherbuliez and H. Weniger, *Helv. Chim. Acta*, **28**, 1584 (1945).
(3) E. Cherbuliez and J. P. Leber, *ibid.*, **35**, 644 (1952).
(4) E. Cherbuliez and H. Weniger, *ibid.*, **29**, 2006 (1946).
(5) E. Cherbuliez and J. Rabinowitz, *ibid.*, **39**, 1455 (1956).
(6) R. M. McReady and W. Z. Hassid, *J. Am. Chem. Soc.*, **66**, 560 (1944).
(7) D. C. Stewart and H. W. Crandall, *ibid.*, **73**, 1377 (1951).
(8) R. H. A. Plimmer and W. J. N. Burch, *J. Chem. Soc.*, 279, 292 (1929).
(9) K. Dimroth and R. Ploch, *Chem. Ber.*, **90**, 801 (1957).
(10) P. R. Hammond, *J. Chem. Soc.*, 2521 (1962).
(11) D. A. Brown, T. Malkin and G. K. Maliphant, *ibid.*, 1584 (1955).

orthophosphates have been detected both in the course of the alcoholysis and as a constituent in crude monoalkyl phosphates. Their presence may be demonstrated qualitatively by means of a paper chromatographic method performed essentially as described by Hanes and Isherwood.[12] These compounds result from a competing reaction, the direct esterification of pyrophosphoric acid, eq. 2.

$$H_4P_2O_7 + ROH = RH_3P_2O_7 + HOH \qquad (2)$$
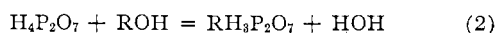
The monoalkyl pyrophosphate, once formed, may be

$$RH_3P_2O_7 + ROH = R_2H_2P_2O_7 + HOH \qquad (3)$$
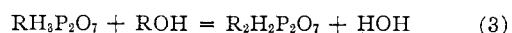
esterified, according to eq. 3, or alcoholyzed in one of two ways, according to eq. 4 and 5.

$$RH_3P_2O_7 + ROH = R_2HPO_4 + H_3PO_4 \qquad (4)$$

$$RH_3P_2O_7 + ROH = 2RH_2PO_4 \qquad (5)$$
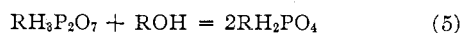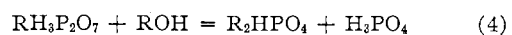
The small amount of monoalkyl pyrophosphate present in a reaction solution may be converted to monoalkyl orthophosphate and orthophosphoric acid in the work-up procedure. In the mono-2-ethylhexyl phosphate preparation, the reaction solution was dissolved in benzene and the resulting solution extracted once with water to remove the bulk of the inorganic acids. Then a second extraction at 70°, the reflux temperature of the two-phase system, was carried out with continuous stirring for several hours. This effected the hydrolysis of mono-2-ethylhexyl pyrophosphate

$$C_8H_{17}H_3P_2O_7 + H_2O = C_8H_{17}H_2PO_4 + H_3PO_4 \qquad (6)$$

and its virtual elimination from the organic layer was demonstrated by paper chromatography. In the case of solid monoalkyl phosphate all other organic phosphates are eliminated expediently by recrystallization.

Experimental

Chemicals.—With the exception of 2-ethylhexanol, alcohols were Eastman Organic Chemicals White Label grade which were used without further purification. The 2-ethylhexanol was a distilled commercial product. Pyrophosphoric acid was provided by the Semi-Works Department of the Victor Chemical Division of the Stauffer Chemical Company. Its preparation and properties have been outlined by Malowan.[13] Although this compound is very hygroscopic, it may be handled in air without provision for exclusion of moisture if operations are carried out rather swiftly. The pyrophosphoric acid used contained less than 2% of other phosphoric acids, mainly orthophosphoric acid. Benzene used as a solvent was distilled from phosphorus(V) oxide.

Determination of Extent of Reaction.—The extent of reaction may be determined by means of a titrimetric procedure for orthophosphoric acid in the presence of alkyl phosphates and pyrophosphoric acid. A sample of the liquid phase is withdrawn and dissolved in 75% acetone–25% water, by volume. The titration with 0.1 N NaOH is carried through the first end point A at pH 5 to 7 and the second end point B at pH 9.5 to 11.5. When end point B has been passed, 25 ml. of 10% barium chloride is added, releasing the third hydrogen of orthophosphoric acid. The pH is adjusted to about 11.5 with excess 0.1 N NaOH and a back titration with 0.1 N HCl to a strong hydrogen end point at pH 8 to 11 gives the third end point C. The total phosphorus content is calculated from end point A. The number of equivalents of

base used beyond end point B minus the number of equivalents of acid used to reach end point C gives the orthophosphoric acid content. Thus, the method allows direct determination of orthophosphoric acid and total phosphorus with good accuracy.

As an example, the conversion of 2-ethylhexanol to mono-2-ethylhexyl phosphate and orthophosphoric acid was followed. The reaction was initiated by addition of 55.7 g. (0.313 mole) of pyrophosphoric acid to a solution of 32.5 g. (0.250 mole) of 2-ethylhexanol and 100 g. of benzene in a 250-ml. three-necked reaction flask fitted with a high speed Waco stirrer and thermometer. No provision was made for temperature control but it remained between 27 and 29° throughout the reaction. Pertinent results are tabulated in Table I.

TABLE I

Time, hr.	% P, liq. phase	% of P in liq. phase as H_3PO_4
0.0	...	...
0.62	6.92	...
2.66	8.43	...
4.87	9.20	22.2
10.6	9.20	27.6
22.8	9.06	37.5
49.2	9.23	38.5
70.5	9.11	39.2
93.5	9.28	40.9

A small amount of pyrophosphoric acid remained undissolved. Accepting an average phosphorus content of 9.2%, which includes some soluble excess pyrophosphoric acid, the percentage of phosphorus as orthophosphoric acid would reach about 47% for completion of the reaction

$$H_4P_2O_7 + C_8H_{17}OH = C_8H_{17}H_2PO_4 + H_3PO_4 \qquad (7)$$

to the right. Since substantially the same rates of reaction were found using *n*-decyl alcohol and *n*-dodecyl alcohol in identical experiments a reaction time of about 30 hr. would be convenient for synthetic purposes.

Identification and Analysis of Products.—Both crude and purified products were analyzed by the titration procedure described above. For purified products it was found that the difference 2A − B was equal to zero, indicating the absence of both dialkyl orthophosphate and monoalkyl pyrophosphate. The results were confirmed qualitatively by means of a paper chromatographic method.[12] In the chain length range studied, resolution of orthophosphoric acid, pyrophosphoric acid, and monoalkyl phosphate was possible using as a chromatographic solvent a solution containing 60% acetone, 35% water, and 5% concentrated ammonia, by volume. For resolution of monoalkyl phosphate, dialkyl phosphate, monoalkyl pyrophosphate, and dialkyl pyrophosphate a solvent containing 80% acetone, 15% water, and 5% concentrated ammonia was used. The virtual absence of orthophosphoric acid from purified products was demonstrated both by paper chromatography and titration.

Preparation of Mono-2-ethylhexyl Phosphate.—Pyrophosphoric acid (138 g., 0.830 mole) and 2-ethylhexanol (91.8 g., 0.706 mole) were added to a 500-ml. flask. After stirring until a clear solution formed the flask was allowed to stand for 2 days. A portion of the liquid (96.5 g.) was dissolved in 200 ml. of benzene. One extraction with 100 ml. of water was followed by a 4-hr. extraction with 100 ml. of water at the reflux temperature of 70°, with continuous stirring. This procedure effected the hydrolysis of a small amount of mono-2-ethylhexyl pyrophosphate formed by direct esterification of pyrophosphoric acid. The benzene layer was added to a solution prepared from 50 g. of 50% NaOH and 500 ml. of water. Unreacted alcohol (6.9 g.) was recovered from the benzene layer. The aqueous layer was adjusted to pH 0.5 with concentrated HCl. At this point 200 ml. of ether was added to dissolve the monoalkyl phosphate formed. The ether solution was washed once with 1 N HCl and once with water. After evaporation of ether the product contained 2.9%

(12) C. S. Hanes and F. A. Isherwood, *Nature*, **164**, 1107 (1949).

(13) J. E. Malowan, *Inorg. Syn.*, **3**, 96 (1950).

water, which was removed by passing a stream of dry air through the liquid for 24 hr. The product, a viscous water-white liquid, weighed 38.6 g., corresponding to a yield 77% of theoretical based upon the weight of alcohol consumed. The purity of the product was ascertained by titration and chromatography. *Anal.* Calcd. for $C_8H_{17}H_2PO_4$: P, 14.7; equiv. wt., 210. Found: P, 14.3; equiv. wt., 204; $n^{25}D$ 1.4411.

Preparation of Mono-*n*-decyl Phosphate.—Pyrophosphoric acid (111 g., 0.625 mole), *n*-decyl alcohol (79.0 g., 0.500 mole), and benzene (100 g.) were added to a 500-ml. flask. After stirring until a clear solution formed, the flask was allowed to stand for 4 days. A portion (138 g.) of the viscous liquid produced was dissolved in 300 ml. of ether. In extraction procedures, ether is preferred over benzene since monoalkyl phosphates show a lesser tendency toward emulsification in ether. The ether solution was extracted once with 200 ml. of water. The ether-rich layer then was added dropwise with stirring to a solution prepared from 500 ml. of water and 60 g. of 50% NaOH. During the addition, 100 ml. of ether also was added to reduce viscosity. From the resulting ether-rich layer 4.0 g. of *n*-decanol was recovered. The pH of the aqueous layer was adjusted from an initial 12.4 to a final 0.5 with concentrated HCl. During the acidification the formation and dissolution of both $C_{10}H_{21}NaHPO_4$ and $C_{10}H_{21}NaHPO_4 \cdot$

$C_{10}H_{21}H_2PO_4$ was observed. These salts were not isolated as their preparation by neutralization of alcoholic monoalkyl phosphates has been described previously.[11] At pH 0.5, 300 ml. of ether was added with the formation of two liquid layers. The aqueous layer was discarded. The ether-rich layer was washed with 1 *N* HCl and transferred to an evaporating dish. After evaporation of the ether, the crude product was vacuum desiccated over sulfuric acid. The crude product weighed 47.1 g., 94% of the expected yield based upon the quantity of alcohol consumed. Recrystallization from hexane gave a white, crystalline product containing no other decyl phosphates. *Anal.* Calcd. for $C_{10}H_{21}H_2PO_4$: P, 13.0; equiv. wt., 238. Found: P, 12.9; equiv. wt., 236; m.p. 45°.

The following compounds were prepared in a similar manner: **Mono-*n*-dodecyl phosphate:** yield, 100%. *Anal.* Calcd. for $C_{12}H_{25}H_2PO_4$: P, 11.65; equiv. wt., 266. Found: P, 11.6; equiv. wt., 265; m.p. 58°. **Mono-*n*-tetradecyl phosphate:** yield, 92%. *Anal.* Calcd. for $C_{14}H_{29}H_2PO_4$: P, 10.5; equiv. wt., 294. Found: P, 10.8; equiv. wt., 302; m.p. 68°.

Nature of Bonding in Metal Cyanide Complexes as Related to Intensity and Frequency of Infrared Absorption Spectra[1]

BY LLEWELLYN H. JONES

The frequencies of the infrared-active CN stretching, MC stretching, and MCN bending vibrations of several metal–hexacyanide complexes have been observed in aqueous solution. The integrated absorption coefficients of the CN stretching vibrations increase regularly with the number of d_ϵ electrons. These intensity and frequency data together show that the extent of metal–cyanide π-bonding increases as the number of d_ϵ electrons increases and as the effective nuclear kernel charge decreases. The carbon–nitrogen force constant is shown to increase with increase in metal–cyanide σ-bonding and decrease in metal–cyanide π-bonding. The linear dicyanides of Ag(I), Au(I), and Hg(II) are shown to fit into this picture also.

Introduction

In the past few years much has been written on the nature of bonding in metal–cyanide complexes, perhaps the most recent being a review by Griffith.[2] Part of his discussion concerns the relation of MC and CN force constants to the nature of σ-bonding and π-bonding in the complex. However, a good share of the reported force constants for the metal–carbon bonds are subject to considerable doubt. For instance, Griffith[2] quotes Pistorius'[3] value for F_{MC} of $Ni(CN)_4^{-2}$ as 3.42 mdynes/Å. while McCullough, *et al.*,[4] in a more detailed study, report F_{MC} as 2.6 mdynes/Å. Also Griffith[2] reports for $Co(CN)_6^{-3}$ Nakagawa's and Shimanouchi's[5] value for F_{CoC} of 2.31 mdynes/Å. whereas Jones[6] gives F_{CoC} equals 1.8 mdynes/Å. Thus it is difficult to base a theory of bonding on this evidence.

Another source of information, too often neglected, on the bonding in complexes, is the observation of intensities of the vibrational absorption bands. From these intensities information can be obtained about the rearrangement of electrons accompanying changes of configuration and thus an insight into the nature of the equilibrium electronic configurations is available. In this paper the intensities of absorption of several metal–cyanide complexes are compared and related to electronic distribution and bonding properties.

Experimental

The absorption bands discussed in this paper were measured in aqueous solution. For the CN stretching region a fixed-thickness cell with 2-mil tantalum spacer and calcium fluoride windows was used with a Perkin-Elmer Model 421 spectrometer. From the spacing of interference peaks in the infrared region, the thickness was determined to be 0.0062 cm. A cell of the same thickness containing water only was used in the reference beam to cancel out the solvent absorption.

The two infrared-active fundamentals in the region 300–600 cm.$^{-1}$ were recorded by a single-beam Perkin-Elmer Model 112 spectrometer with a CsBr prism. The cells used for this region contained KRS5 windows and tantalum spacers of 0.2 mil

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) W. P. Griffith, *Quart. Rev.* (London), **16**, 188 (1962).

(3) C. W. F. T. Pistorius, *Z. physik. Chem.* (Leipzig), **23**, 200 (1960).

(4) R. McCullough, L. Jones, and G. A. Crosby, *Spectrochim. Acta*, **16**, 424 (1960).

(5) I. Nakagawa and T. Shimanouchi, *ibid.*, **18**, 101 (1962).

(6) L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).