Bull. Environm. Contam. Toxicol. 25, 755-761 (1980)

Characterization of Four Commercial Flame Retardant Aryl Phosphates

Ellyn R. Nobile, Samuel W. Page, and Pasquale Lombardo
Division of Chemical Technology, Food and Drug Administration,
Washington, DC 20204

Aryl phosphates are widely used as flame retardant plasticizers and fire resistant hydraulic fluids. Their volume of production is approximately 100 million pounds per year (MRI 1977). Information about the chronic toxicity of most of these compounds is limited, although several are known to be delayed neurotoxins (JOHNSON 1975).

The commercial products are generally isomeric mixtures of phosphate esters based on phenols such as phenol itself, cresols, xylenols, nonylphenol, cumylphenol, and isopropylphenols. Information on their specific chemical compositions is generally unavailable, although some data have been reported (MURRAY 1975).

Large amounts of aryl phosphates may be released directly into the aquatic environment through leakage of hydraulic machinery. Residues of phosphate esters have recently been reported to be present in fish collected near users of hydraulic fluids (MURRAY 1975, LOMBARDO & EGRY 1979). Once the commercial mixtures are exposed to the environment, the proportions of their components may be altered, depending on the fate of the individual compounds. Individual reference phosphates are needed for identifying and quantitating such altered residues in environmental samples.

Several products based primarily on phenol, cresols, nonylphenol, and cumylphenol have previously been examined (MURRAY 1975, LOMBARDO & EGRY 1979, DEO & HOWARD 1978). We chose to analyze four commercially important products (Kronitex 100, Kronitex 50, Fyrquell 220, Kronitex TXP) representing the isopropylphenyl and xylenyl types of phosphates used both as hydraulic fluids and plasticizers, since little has been published on their specific compositions.

EXPERIMENTAL

Commercial Aryl Phosphates Examined. Kronitex 100, Kronitex 50, and Kronitex TXP, all flame retardant plasticizers, were obtained by courtesy of the FMC Corporation, Philadelphia, PA. Fyrquell 220, a fire resistant hydraulic fluid manufactured by

0007-4861/80/0025-0755 $01.40

Stauffer Chemical Company, was obtained from Mr. John Hesse, Michigan Department of Natural Resources, Lansing, Mich.

Analysis of Hydrolysis Products. Typically, several grams of each product were dissolved in 100 mL of methanol and mixed with a solution of 30 g of NaOH in 50 mL of water. The mixture was heated at reflux for several hours. After cooling, the solution was acidified with concentrated HCl and extracted four times with 50 mL portions of ethyl acetate. The combined organic layers were washed with 10% (v/v) HCl and dried over anhydrous Na_2SO_4. The organic solution was filtered and the solvent was removed under reduced pressure. An aliquot of the hydrolyzate was removed and characterized by infrared spectrophotometry (IR), gas-liquid chromatography (GLC), GLC-mass spectrometry (MS), and nuclear magnetic resonance (NMR). Compounds were identified by comparison of their GLC retention times with those of standards and by GLC-MS data. The difficulty of separating the phenols by GLC hindered our attempts at precise quantitation. Several GLC columns were tried in an attempt to resolve the various isomers. One type, a 5% Bentone + 20% OV-101 on Chromosorb W-HP, looked encouraging; unfortunately we were unable to duplicate the separations with other columns having the same apparent composition. We did not spend additional time attempting to quantitate the minor constituents of the hydrolyzate, since the main objective was to determine the identity of the major isomeric phenols to provide adequate information for preparing the individual phosphate standards.

Synthesis of Aryl Phosphate standards. Molar amounts of the various individual isomeric phenols were reacted with phosphorus oxychloride, diphenylchlorophosphate, or phenyldichlorophosphate in toluene and refluxed 4-6 h in the presence of excess triethylamine. This mixture was cooled and washed four times with 10% (v/v) HCl. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. The individual phosphates were characterized by IR, GLC, GLC-MS, NMR, and high performance liquid chromatography (HPLC), and are listed in Table I by relative GLC retention times on a 3% OV-101 column.

RESULTS AND DISCUSSION

Kronitex 100 and Kronitex 50. Qualitatively, the constituents of the hydrolysis products were the same. The principal products in order of abundance were phenol, 2-isopropylphenol, and 4-isopropylphenol; these accounted for at least 80% of the phenols. GLC-MS analysis indicated that diisopropylphenols accounted for the bulk of the other phosphate precursors. Three of the possible six diisopropylphenols (2,6-, 2,5-, 3,5-) were commercially available, but their retention times did not match any of those observed in the hydrolyzate. A small amount of 3-isopropylphenol was also detected.

TABLE I

GLC Retention Times of Individual Phosphates Prepared

Phosphate	Relative retention time [a]
[triphenyl]	1.00
diphenyl 2-isopropylphenyl	1.49
phenyl di-(2-isopropylphenyl)	2.15
diphenyl 4-isopropylphenyl	2.15
tris-(2-isopropylphenyl)	3.1
tris-(2,5-xylenyl)	3.3
tris-(3,5-xylenyl)	4.0
tris-(2,4-xylenyl)	4.3
phenyl di-(4-isopropylphenyl)	4.6
tris-(4-isopropylphenyl)	9.8

[a] The retention times are relative to triphenylphosphate (4.1 min.) GLC parameters: 6 ft X 2 mm i.d. coiled glass column packed with 3% OV-101 on 80/100 mesh Chromosorb W-HP, injector 250°C, column 220 °C, N_2 carrier gas 30 mL/min, flame ionization detector.

GLC chromatograms of the commercial products are illustrated in Figure I and the major components are listed in Table II. The quantity of each component was determined by GLC peak height comparisons with individual standards. Diphenyl 4-isopropylphenyl phosphate and phenyl di-(2-isopropylphenyl) phosphate co-eluted on the GLC column used. However, they were separated and quantitated in the mixtures by HPLC (C_{18} reverse phase column; water-methanol gradient). The relative proportions of triphenylphosphate and diphenyl 2-isopropylphenyl phosphate were quite different in the two products examined. We assumed that the aryl phosphate mixtures sampled are representative of the commercial products, but realize that the relative proportions of the compounds contained in these mixtures may vary from lot to lot.

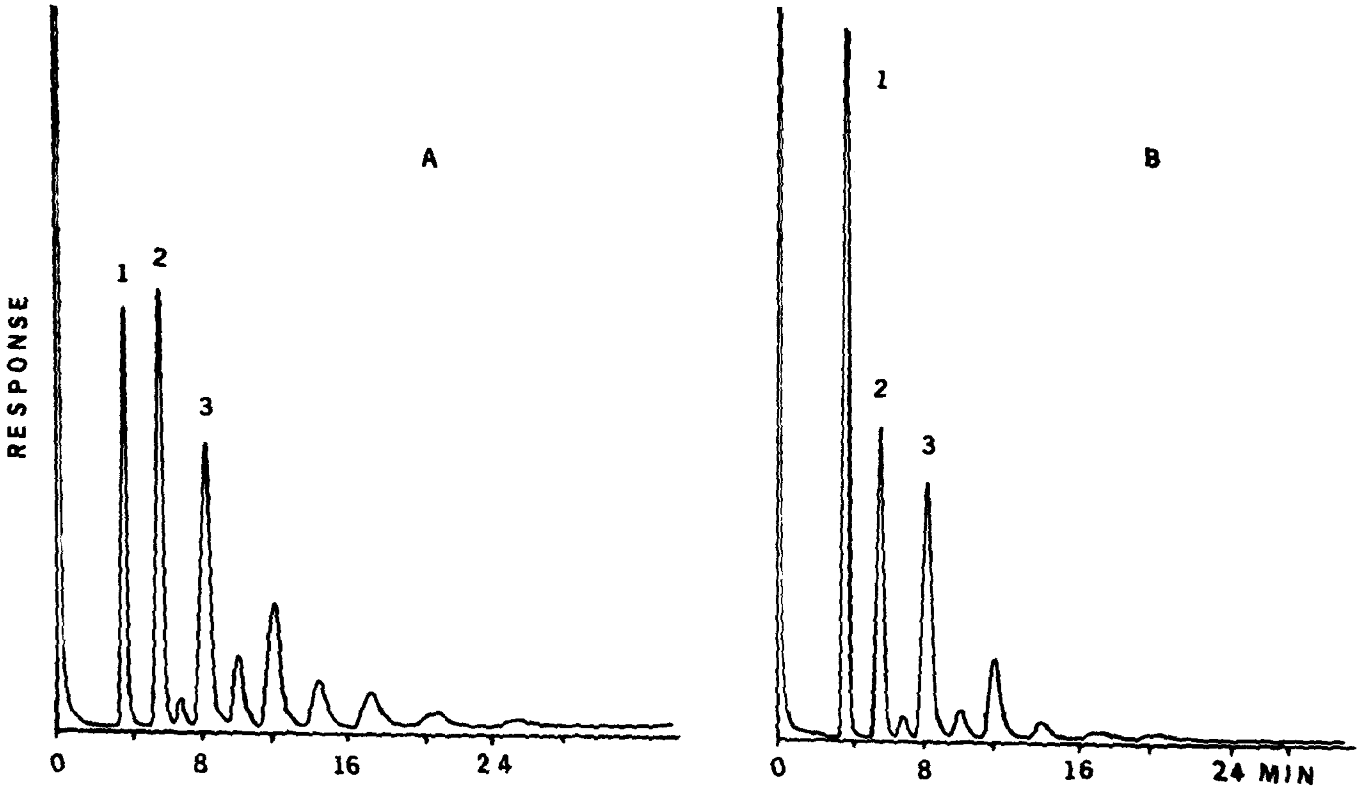

Figure 1. Gas-liquid chromatograms of Kronitex 100 (A) and Kronitex 50 (*B*). *Conditions:* 6 ft X 2 mm 3% OV-101 operated at 220° C, N_2 carrier 30 mL/min, flame ionization detector. Triphenyl phosphate (1), diphenyl 2-isopropylphenyl phosphate (2), diphenyl 4-isopropylphenyl phosphate/phenyl di-(2-isopropylphenyl) phosphate (3).

TABLE II

Major Components of Kronitex 100 and Kronitex 50

Phosphate	Kronitex 100 %	Kronitex 50 %
triphenyl	18	33
diphenyl 2-isopropylphenyl	27	21
diphenyl 4-isopropylphenyl	11	12
tris-(2-isopropylphenyl)	11	8
phenyl di-(2-isopropylphenyl)	7	6
phenyl di-(4-isopropylphenyl)	5	2
Total [a]	79	82

[a] Other components were observed, but were not identified or quantitated.

Fyrquell 220 and Kronitex TXP. Hydrolysis yielded similar mixtures of xylenols, ethylphenols, and phenol. Proton NMR spectroscopy was useful in identifying ethylphenol and xylenol isomers, all of which have similar mass spectra. Xylenols accounted for the bulk of the hydrolysis products; they were, in order of abundance, the 2,5-, 2,3-, 3,5-, 2,4- and 3,4-isomers. The 2,6-isomer was not detected. The remaining hydrolysis products identified were 4-ethylphenol, p-cresol, phenol, and trimethylphenol.

The gas chromatograms of these commercial mixtures are illustrated in Figure 2. Tris-(2,5-xylenyl) phosphate was present in both products. As tris-(3,5-xylenyl) and tris-(2,4-xylenyl) phosphates co-eluted, either one or both may be present. These comercial mixtures gave a much more complex GLC pattern than Kronitex 100 or Kronitex 50, and their components were extremely difficult to separate. Other GLC packed columns (OV-17, Silar, Carbowax 20M) were tried without success. No attempts were made to identify the remaining components, which may be mixed xylenyl phosphates or xylenyl/ethylphenyl phosphates, because they could not be resolved sufficiently.

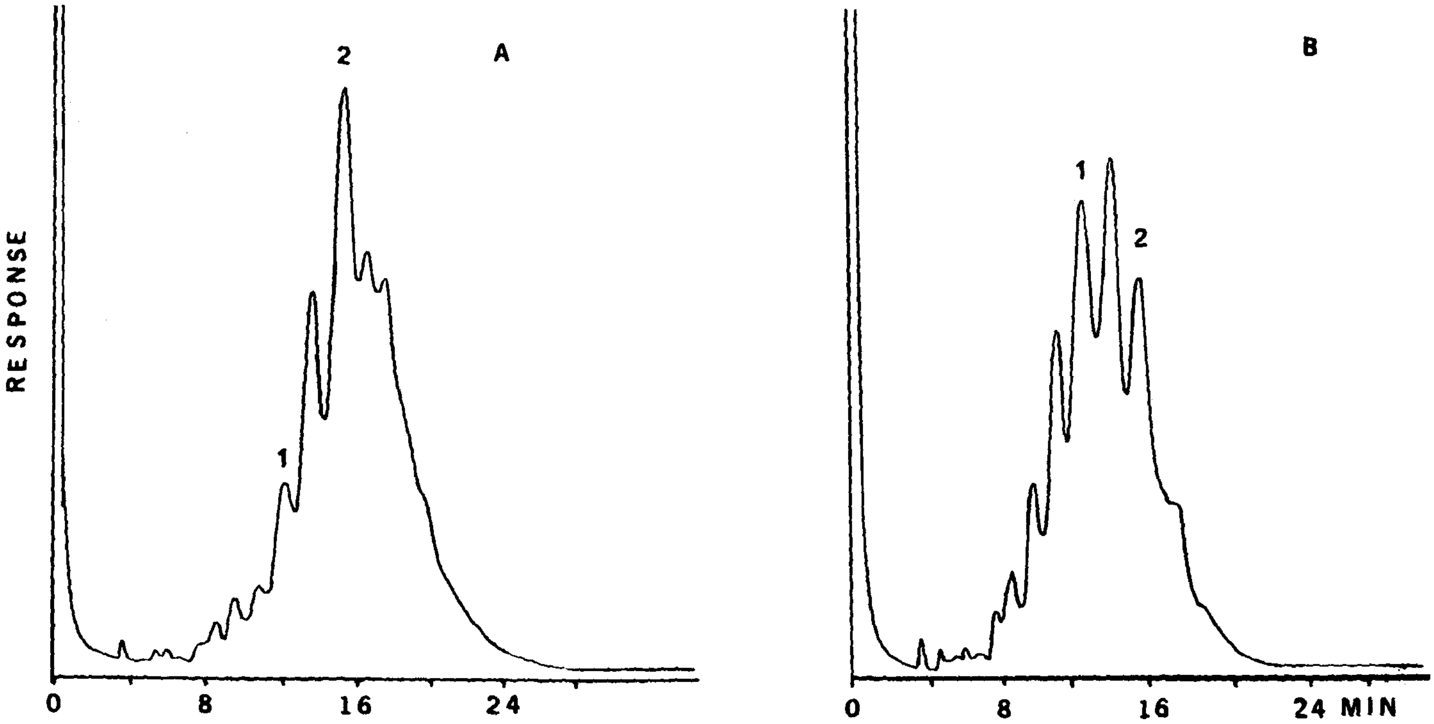

Figure 2. Gas-liquid chromatograms of Fyrquell 220 (A) and Kronitex TXP (B). Conditions: 6 ft X 2 mm 3% OV-101 column operated at 220°C, N_2 carrier 30 mL/min, flame ionization detector. Tris-(2,5-xylenyl) phosphate (1), tris-(3,5-xylenyl) phosphate and/or tris-(2,4-xylenyl) phosphate (2).

ACKNOWLEDGEMENT

The authors thank James A. Poppiti for obtaining the mass spectra.

REFERENCES

DEO, P. G. and P. H. HOWARD: J. Assoc. Off. Anal. Chem. 61, 266 (1978).

JOHNSON, M. K. : CRC Crit. Rev. Toxicol. 3, 289 (1975).

LOMBARDO, P. and I.J. EGRY: J. Assoc. Off. Anal. Chem. 62, 47 (1979).

MIDWEST RESEARCH INSTITUTE: Assessment of the Need for, the Character of, and the Impact from Limitations of Aryl Phosphates, Draft Final Report. Washington, DC. EPA # 68-01-4313 (1977).

MURRAY, D.A.J.: J. Fish Res. Board Can., 32, 457-460 (1975).

This paper was presented at the 92nd Annual Meeting of the Association of Official Analytical Chemists, October 16-19, 1978, in Washington, DC.