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Degradation of Aryl Phosphates in Aquatic Environments

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Approximately 90 million pounds of aryl phosphates are annually produced for use as fire resistant plasticizers and hydraulic fluids (MIDWEST RESEARCH INSTITUTE 1977). This large volume is likely to result in release to the environment either from losses during manufacture or use (especially use of hydraulic fluids). A significant loss of some aryl phosphate hydraulic fluid used in a small steel mill to a Pennsylvania river has recently been noted by the Pennsylvania Department of Environmental Resources (SCHAEFFER 1977). Because of the possible widespread contamination of water systems by aryl phosphates, it is important to understand the fate of these compounds in aqueous media.

Several investigators have studied the hydrolysis rates of aryl phosphates, but in most cases the conditions used were not similar to conditions in nature. BARNARD et al. (1961) found that the pseudo-first-order rate constant of triphenyl phosphate in dioxane-water (3:1 V/V) at 100°C was 6.0×10^{-8} sec^{-1} (half-life 130 days), while the second-order rate constant under alkaline conditions in dioxane-water mixture (3:1 V/V) at 24.7°C was 0.0106 l $mole^{-1}$ sec^{-1}. The latter value was experimentally determined at pH 13 but should apply to all alkaline conditions. Using this value, the calculated half-lives in that solvent system at pH 9.5 and 8.2 are 23 and 472 days, respectively, at 24.7°C. These rate constants only apply to the first hydrolysis step converting triphenyl phosphate to diphenyl phosphate, since the hydrolysis rate of diphenyl phosphate under acid and alkaline conditions is extremely slow [at 100°C, pH 7.47, in water the pseudo-first-order rate constant is 6×10^{-9} sec^{-1} (BARNARD et al. 1966)]. The hydrolysis of triaryl phosphates under slightly acid conditions has not been studied, although strong acid rate constants have been determined (BARNARD et al. 1966). By analogy with pesticide organophosphates, it is likely that the hydrolysis of triaryl phosphates under neutral or slightly acid conditions would be extremely slow in nature (WOLFE et al. 1977).

In demineralized river water and in natural river water and sediment WAGEMAN et al. (1974) have studied

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the rate of degradation of a commercial mixture of triaryl phosphates (IMOL S-140) by following the phosphate production. They reported half-lives of 52 to 140 days, depending upon the conditions (demineralized water = 73 days). The starting pH was 7-8 and with time it decreased to 5.6-6.0.

Because of the commercial importance of triaryl phosphates and their likely release to the environment, we have investigated further the hydrolysis of these compounds under acid, neutral, and basic conditions in distilled water and in some alkaline natural waters.

MATERIALS AND METHODS

Instrumental - Gas liquid chromatography (GLC) was carried out on a Tracor MT 220 Gas Chromatograph equipped with flame photometric detector supplied with a 526 nm filter (P-mode) and fitted with a Pyrex 1.27 cm x 1.82 m U-shaped column packed with 3% OV-101 on 80-100 mesh Chromasorb WHP obtained from Supelco, Inc., Bellefonte, Pennsylvania. Gas flow rates (ml/min) were: hydrogen, 75; air, 80; nitrogen (carrier gas), 125; and the temperatures for injector, detector, and column were 225, 200, and 215, respectively.

Gas liquid chromatography/mass spectrometry (GLC/MS) analysis was performed with a Finnigan 330 gas liquid chromatograph/mass spectrometer supplied with a System Industries Data Processor. The operating temperature conditions and column were the same as before, but the flow rate of nitrogen was between 1520 ml/min and temperature programming was done from 100-250°C with 10° rise per minute.

Commercial Aryl Phosphates - Triphenyl phosphate (TPP), diphenyl phosphate (DPP), and monophenyl phosphate, and the pure *o*, *m*, or *p*-tricresyl phosphate were obtained from Aldrich Chemical Co., N.J. The following commercial aryl phosphates, produced by the indicated manufacturers, were obtained: a) Kronitex-R (tricresyl phosphate - TCP), F.M.C. Corporation, Philadelphia, Pennsylvania; b) Santicizer-140 (cresyl diphenyl phosphate - CDP), Monsanto Company, St. Louis, Missouri; and c) Phosflex 41-P and Fyrquel GT, Stauffer Chemical Company, Specialty Chemical Division, New York.

Lake/River Water - Lake Onondaga water was collected from the northeast end of the lake at Liverpool, New York. The pH of the water was 7.8. Lake Ontario water was collected from Oswego (New York) at a site about one-half mile west of the university campus. The pH of this water was 8.2. Seneca River water was collected from a site one mile west of the town of Baldwinsville (New York). The pH of this water was 8.2. On arrival at the laboratory, the water was filtered with an

11 micron filter to remove large particles and then refrigerated until use.

Hydrolysis Studies - These were carried out by measuring the disappearance rates of the triaryl phosphates (TAP's). Excess amounts of triphenyl phosphate (TPP), tricresyl phosphates (TCP's), or the commercial aryl phosphates were separately shaken with the buffered distilled water or the unbuffered lake/river waters for two hours, after which they were filtered with an 11 micron filter which should remove most undissolved material but pass through the microorganisms in natural waters. A sample was removed for determination of the TAP's initially present in the filtrate and taken as the saturated solubility of the chemical. The filtrate was incubated on a rotary shaker at room temperature (21 ± 2°C) and samples were removed at intervals for the determination of residual amounts of aryl phosphates. Tributyl phosphate (TBP) was added as an internal standard to the aliquot, which was acidified to pH 1-2 with dilute HCl, NaCl was added until the aliquot was 15% NaCl, and then the aliquot was extracted with ethyl ether. The ether layer was separated, dried with anhydrous Na_2SO_4, concentrated, and treated with diazomethane. The resulting ethereal solution of TAP's, methyl aryl phosphates, and anisoles were diluted to a known volume and determined by GLC with flame photometric detection. Concentrations of the aryl phosphates from their peak area values were determined by using a standard curve of peak area vs. concentration.

Our recoveries of TAP's from all water samples were almost quantitative (90-100%). TBP was added to each sample to determine the recovery and the reported values have been adjusted. Our recoveries of DPP from distilled water were around 70%, but they varied greatly in different samples. The results presented for DPP are based on the amounts which we could extract by our procedure. They were not corrected for recovery (since the recovery is not reproducible) and, therefore, may be subject to considerable error.

Hydrolysis studies under acid conditions were carried out using dilute HCl (pH 4-5). For basic degradation studies at pH 9.5 and 8.2, boric acid-sodium hydroxide and sodium dihydrogen phosphate-disodium hydrogen phosphate buffers were used, respectively (WOLFE et al. 1977). Degradation studies at neutral pH were carried out in distilled water. Hydrolysis studies in natural waters were carried out without any pH control after they were filtered.

RESULTS AND DISCUSSION

Figure 1 presents the results obtained for the disappearance of triphenyl phosphate (TPP) and the formation of diphenyl phosphate (DPP) at room temperature. The slope of the lines is proportional to the rate constants. The disappearance plots very clearly indicate that the hydrolysis rates of TPP are much faster in alkaline conditions than those in neutral or acid conditions. The half-lives at pH 9.5 and 8.2 were 1.3 days and 7.5 days, respectively. Degradation rates under neutral and acid conditions were too slow to reliably measure the rate constants. Figure 1 also illustrates the pH dependence of the alkaline hydrolysis which is consistent with the second-order reaction mechanism (SN_2 attack at phosphorous) which has been frequently proposed for alkaline hydrolysis of organophosphate esters (BUNTON 1970). The increase in the hydrolysis rate with increase in pH has been observed for a variety of organophosphate esters (BARNARD *et al.* 1961; WOLFE *et al.* 1977; GOMOA and FAUST 1972).

The hydrolysis rates are within reason relative to the results of BARNARD *et al.* (1961) who used a dioxane-water (3:1 V/V) media. The calculated alkaline half-lives (23 and 472 days for TPP at 24.7°C and pH's of 9.5 and 8.2, respectively) were considerably higher than our experimental values.

Figure 1 also presents data on the formation of diphenyl phosphate under the two alkaline conditions. Although the data points are scattered because of poor reproducibility in the extraction procedure, the results indicate that diphenyl phosphate is formed faster at higher pH which is expected from the disappearance kinetics. The analytical procedure used would also have detected monophenyl phosphate and its lack of detection (although recoveries were not good) is consistent with the stability of diphenyl phosphate under acid and alkaline conditions (BARNARD *et al.* 1966).

Figure 2 presents the disappearance rates for triphenyl phosphate in some alkaline natural waters. Triphenyl phosphate appears to be less soluble in these natural waters (0.2-0.3 ppm) than in buffered distilled water (1.4-1.6 ppm). The disappearance rates for all three natural waters are interesting in that very little degradation occurs for the first two days, but then a very rapid loss occurs at a rate that is faster than in distilled water at comparable pH. For example, after two days the pseudo-first-order rate constant for Lake Ontario (initial pH 8.2) is 0.64 $days^{-1}$, while for the Seneca River (initial pH 8.2) the rate constant is 0.34 $days^{-1}$. However, the pseudo-first-order rate constant for buffered distilled water at pH 8.2 is

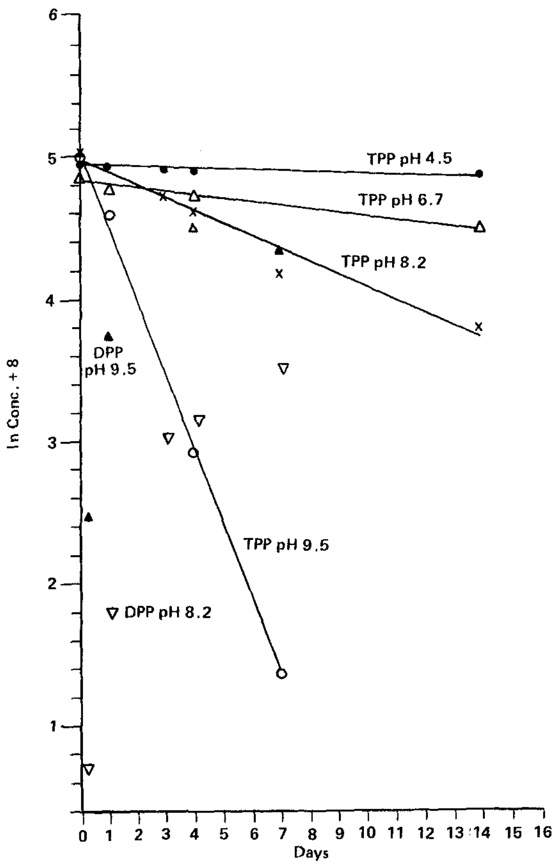

Figure 1. Triphenyl Phosphate (TPP) Loss and Diphenyl Phosphate (DPP) Appearance in Distilled Water

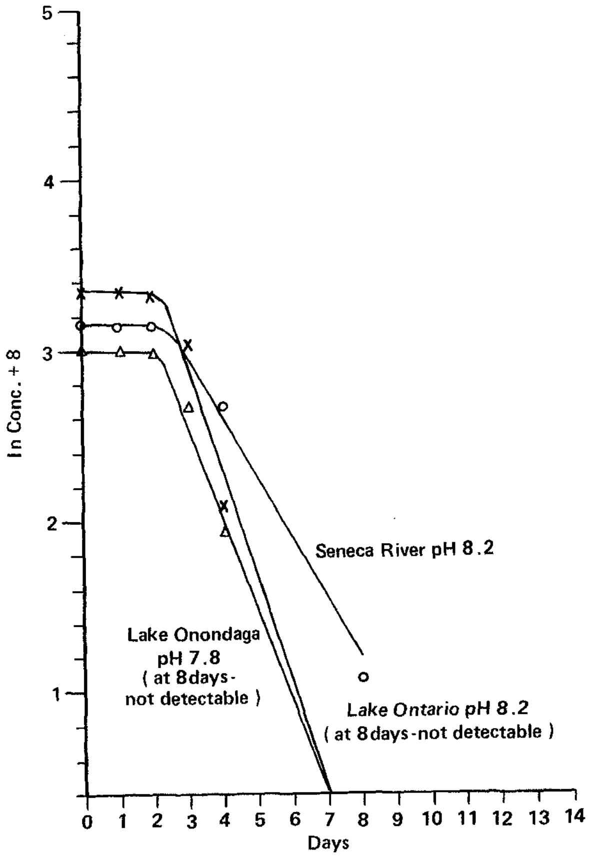

Figure 2. Disappearance of Triphenyl Phosphate (TPP) from Lake and River Waters

0.093 days^{-1}. Some of the difference between distilled and natural waters may be due to temperature differences, since the temperature was not exactly the same (21 ± 2°C) for the distilled and natural water runs. However, all the natural water runs were run under the same conditions so that temperature cannot explain the difference between the Lake Ontario and Seneca River results. The reason for the initial delay is unknown. If microbial enzymatic hydrolysis is important as has been observed previously (MUNNECKE 1976), this delay may be required for acclimation. Also micelles of synthetic surfactants in natural waters could be catalyzing the dephosphorylation (BUNTON _et al_. 1969).

The disappearance of pure isomers of tricresyl phosphate in Lake Ontario water has also been studied (Figure 3). Here again, the initial lag period was observed, followed by a rapid disappearance of the tricresyl phosphate. The _ortho_-isomer degraded slightly faster than the _meta_-isomer and both isomers were degraded faster than the _para_-isomer, which degraded about as fast as triphenyl phosphate.

In order to determine if the commercial aryl phosphates degraded in the same manner as the pure aryl phosphates, we studied the degradation (disappearance) of four commercial aryl phosphates by Lake Ontario water (initial pH 8.2) at concentrations equal to their solubilities. Our results (Figure 4) clearly indicate that even the more complex aryl phosphates undergo rapid degradation by lake water. The degradation was slow during the first 48 hours. Nevertheless, all four aryl phosphates tested showed very rapid degradation in the lake water in 5-6 days, with most of the major components disappearing and new compounds with lower retention time being formed.

The methylated ether extract of the water samples containing the commercial aryl phosphates was analyzed by GLC-MS. Considerable change between the GLC-MS of the hydrolyzed and unhydrolyzed (DEO and HOWARD 1977) commercial samples was noted. The GLC-MS of the water samples was extremely complex and contained many interfering hydrocarbons. However, in several of the samples small amounts of the methyl ester of diphenyl phosphate were detected.

Hydrolysis rates determined for commercial samples in our laboratory in natural waters are much faster than inferred by the reported half-lives of 52-140 days for the degradation of IMOL S-140 in Old Krow River water (WAGEMAN _et al_. 1974). The difference between their results and ours may be due to: (a) the use of acid natural waters and (b) the measurement of orthophosphate formed rather than the loss of the triaryl phosphate.

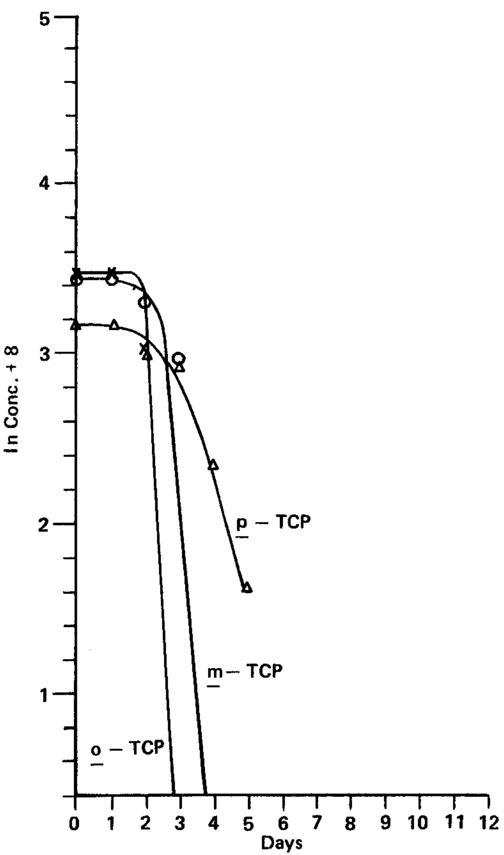

Figure 3. Loss of Tricresyl Phosphate (TCP) Isomers in Lake Ontario Water

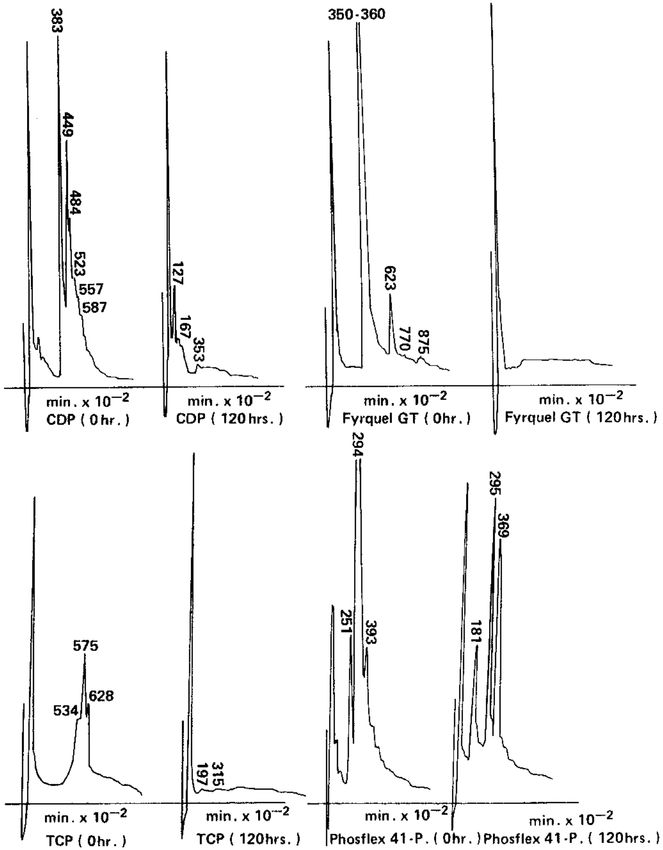

Figure 4. Disappearance of Commercial Aryl Phosphate in Lake Ontario Water (pH 8.2) Using GLC-FPD

In summary, it appears that triaryl phosphates will degrade at appreciable rates in distilled and natural waters under alkaline conditions found in nature to apparently stable, water-soluble products such as diaryl phosphates. The effect of natural water parameters, such as pH, hardness, organic matter, and microbial activity, on aryl phosphate hydrolysis needs to be further studied.

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