

Thermal and spectroscopic characterization of a triaryl phosphate hydraulic fluid

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Abstract The thermal stability of a commercial triaryl phosphate hydraulic fluid has been assessed using thermogravimetry and pyrolysis. This material is a mixture of triaryl phosphates containing a predominance of triphenyl phosphate. It is volatile at higher temperatures. At temperatures below its boiling point, in the presence of air, it slowly decomposes to evolve phenolic fragments.

Keywords Phosphate esters · Thermal stability · Pyrolytic decomposition · Fragmentation · ^{31}P -NMR spectroscopy

Introduction

Hydraulic fluids are required for a wide range of applications (automobiles, aircraft, heavy equipment, industrial processes, and many others). These materials must be thermally and mechanically stable over a range of conditions. Historically, a number of liquids including hydrocarbons, glycols, and emulsions of various types have been used as hydraulic fluids. Among the most useful have been poly(ether)s and triaryl phosphates. Among the poly(ether)s, poly(ethylene oxide), poly(propylene oxide), mixtures of two the polymers, or copolymers of ethylene and propylene oxide have been most widely used [1–6]. Triaryl

phosphate fluids, when compared to competing materials, have several very positive features. They are generally nontoxic, display excellent fire retardancy, have good long-term stability, exhibit excellent lubricity and are readily available by synthesis. A commercial triaryl phosphate fluid, Fryquel EHC, has been characterized using spectroscopic and thermal methods.

Methods and instrumentation

Thermal decomposition was studied using a TA Instruments 2950 Hi-Res TGA instrument interfaced with a Thermal Analyst control unit. For dynamic runs a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ was used. For isothermal experiments, the temperature was ramped to the desired isothermal temperature and held at that point for several hours as appropriate. TA Thermal Advantage software was used for data analysis. Samples (5–10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen or air at $50\text{ cm}^3\text{ min}^{-1}$ during analysis. Large-scale (50 g) decompositions were carried out in a three-necked, round-bottomed flask fitted with a magnetic stirring bar and a Liebig condenser bearing a gas-inlet tube. The sample was stirred at a fixed temperature under a static atmosphere of either nitrogen or air. Periodically, samples were removed for analysis by infrared and proton NMR spectroscopy and by viscometry. Nuclear magnetic resonance (NMR) spectra were obtained using 10 to 25 % solutions in deuteriochloroform and a Varian Mercury 300 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference ($\delta = 0.0$). Infrared (IR) spectra were obtained using thin films between sodium chloride plates and a Nicolet MAGNA-IR

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560 spectrophotometer. Absorptions were recorded in wave numbers (cm^{-1}) and absorption intensities were classified in the usual fashion as very weak (vw), weak (w), medium (m), strong (s) and very strong (vs) relative to the strongest band in the spectrum. Mass spectra were obtained using a Hewlett-Packard 5890A gas chromatograph/mass spectrometer with an ionizing potential of 70 electron volts and temperature programmed elution into the spectrometer inlet (90–200 °C).

Materials

Common solvents and reagents were obtained from ThermoFischer Scientific or the Aldrich Chemical Company. Triaryl phosphate fluid [Fryquel EHC] was supplied by American Chemical Technologies, Inc.

Results and discussion

The stability of a triaryl phosphate fluid, Fryquel EHC, has been examined. The infrared (Fig. 1), carbon C-13 NMR (Fig. 2), and proton H-1) NMR (Fig. 3) spectra of this material are shown below.

As may be seen from the thermogram presented in Fig. 4, the fluid is too volatile to permit a determination of degradation characteristics using thermogravimetry. Based on the shape of the derivative plot, it would appear to be a mixture of at least two major components [7].

This material is actually a mixture of three major components (and several minor components, <5 % of the total) as indicated by both gas chromatography and phosphorus-31 NMR spectroscopy. The chromatogram is displayed in Fig. 5. The chromatogram contains three major peaks at elution times of 11.0 min (22 % of the mixture assuming only three components as determined from peak

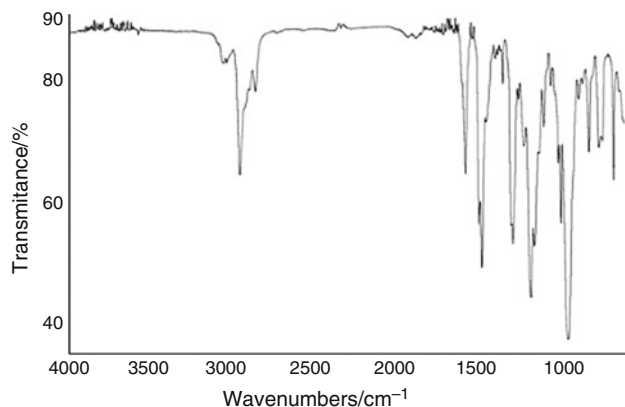


Fig. 1 Infrared spectrum of Fryquel EHC

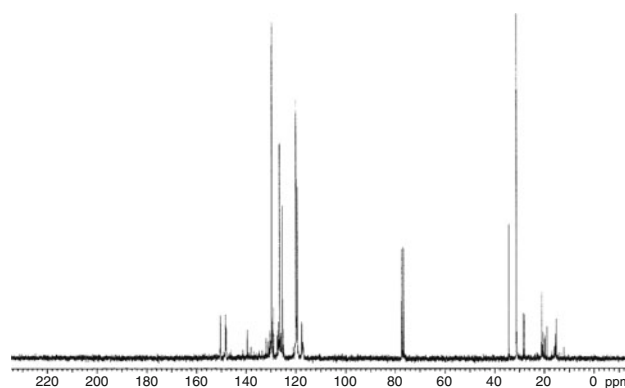


Fig. 2 Carbon-13 NMR spectrum of Fryquel EHC

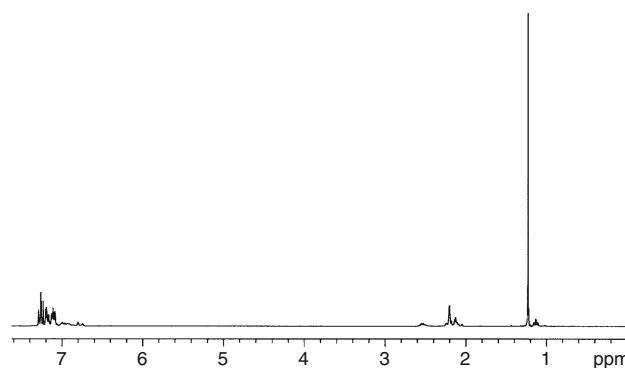


Fig. 3 Proton NMR spectrum of Fryquel EHC

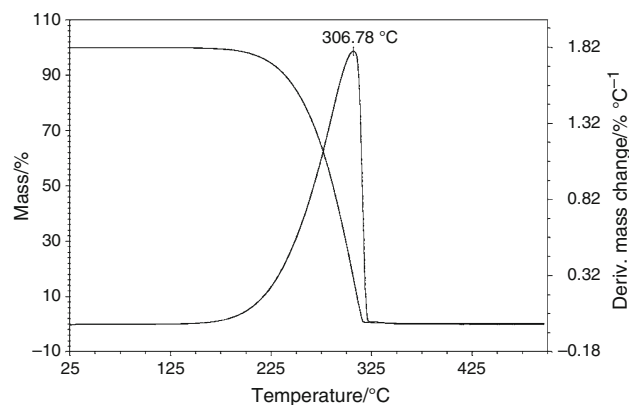


Fig. 4 Volatilization of Fryquel EHC

heights), 12.3 min (50 %) and 13.6 min (28 %). A fourth minor component of the mixture is eluted at 15.4 min. There are also present several small peaks with elution times near 13 min.

The phosphorus-31 NMR spectrum (Fig. 6) of the fluid also suggests that it is a mixture of three major components with resonances at $\delta -17.7$, -18.0 and -18.3 with respect to the absorption for triphenyl phosphate as an internal reference ($\delta -18.0$). A fourth minor compound gives rise to an absorption at $\delta -17.5$.

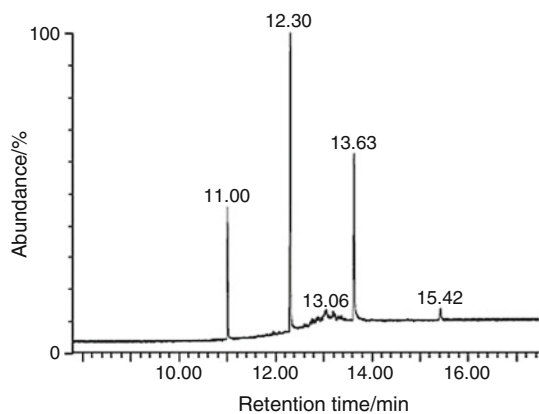


Fig. 5 Gas chromatogram for Fyrquel EHC

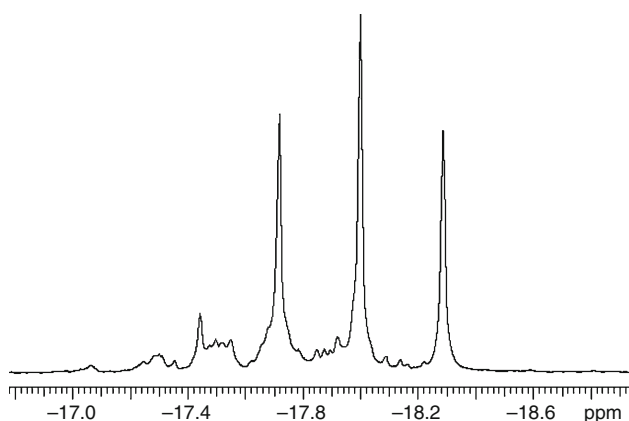


Fig. 6 Phosphorus-31 NMR spectrum of Fyrquel EHC

A tentative identification for the three major compounds is possible from the corresponding mass spectra. The mass spectrum for the compound with a GC retention time of 11.0 min is shown in Fig. 7. The spectrum contains a molecular ion peak at m/z 326 and a significant peak at m/z 325 reflecting the loss of a hydrogen atom. This is what would be expected for triphenyl phosphate.

For comparison the mass spectrum for authentic triphenyl phosphate is shown in Fig. 8. The phosphorus-31

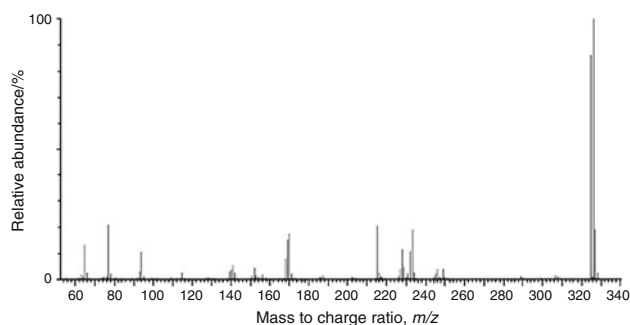


Fig. 7 Mass spectrum of the phosphate ester eluting faster in gas chromatography

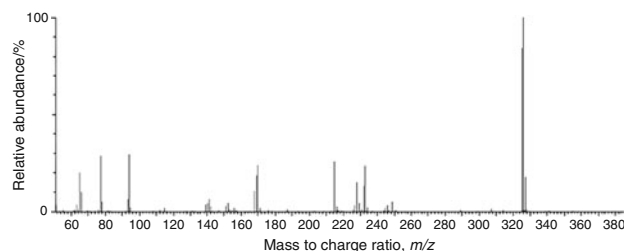
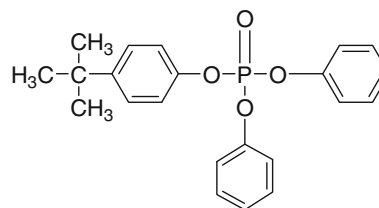


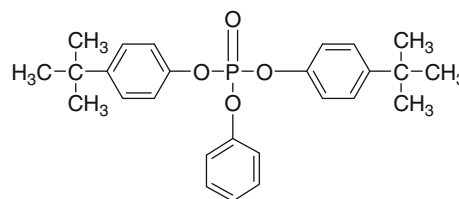
Fig. 8 Mass spectrum of triphenyl phosphate

NMR spectrum of the triphenyl phosphate contains an absorption at δ -18.0. It seems clear that the fastest eluting component ($\sim 22\%$) of the mixture is triphenyl phosphate.

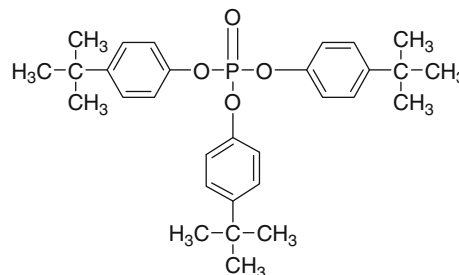
The mass spectrum of the component eluting at 12.5 min contains a molecular ion at m/z 382 with a base peak at m/z 367 (loss of methyl). This is consistent with *t*-butylphenyl diphenyl phosphate for the identity of this compound. The molecular ion would be expected to readily expel a methyl radical to generate a stable tertiary benzylic cation (Fig. 9).



The mass spectrum of the component eluting at 14.8 min contains a molecular ion peak at m/z 438 with a base peak at m/z 423 (loss of methyl). This suggests that this compound is di-*t*-butylphenyl phenyl phosphate (Fig. 10).



The mass spectrum of the minor component eluting at 15.4 min contains a molecular ion peak at m/z 494 with a base peak at m/z 479 suggesting that this compound is tri-*t*-butylphenyl phosphate (Fig. 11).



This analysis is fully supported by the proton (methyl absorption at δ 1.22) and carbon-13 [(absorption for a

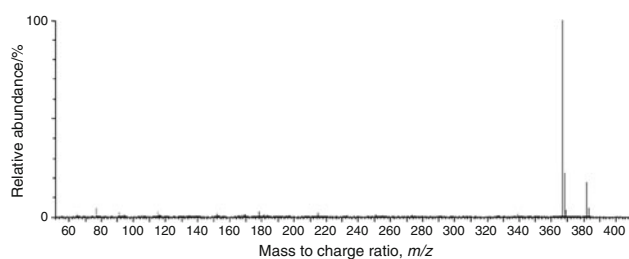


Fig. 9 Mass spectrum of the phosphate ester eluting second in gas chromatography

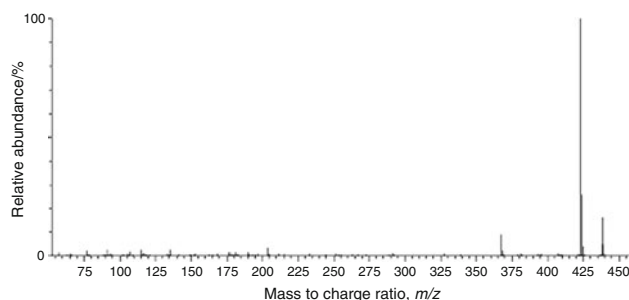


Fig. 10 Mass spectrum of the phosphate ester eluting third in gas chromatography

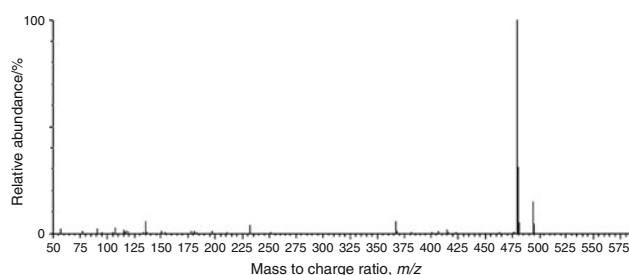


Fig. 11 Mass spectrum of the phosphate ester eluting fourth in gas chromatography

t-butyl group at δ 31.0 (methyl carbon atoms) and δ 34.0 (quaternary carbon atom)] NMR spectra of Fyrquel EHC.

At higher temperature in air Fyrquel EHC does evolve volatile products. The infrared spectrum of the volatile material is displayed in Fig. 12.

The spectrum contains O–H absorption at 3391 cm^{-1} , aromatic ($3063, 3044\text{ cm}^{-1}$) and aliphatic ($2964, 2870\text{ cm}^{-1}$) C–H absorption, absorption for an aromatic nucleus at 1590 cm^{-1} , P–O–C absorption at 1489 and 960 cm^{-1} and $P=O$ absorption at 1189 cm^{-1} . A structure consistent with the infrared data would be that of hydroxyphenyl *t*-butylphenyl phenyl phosphate [8].

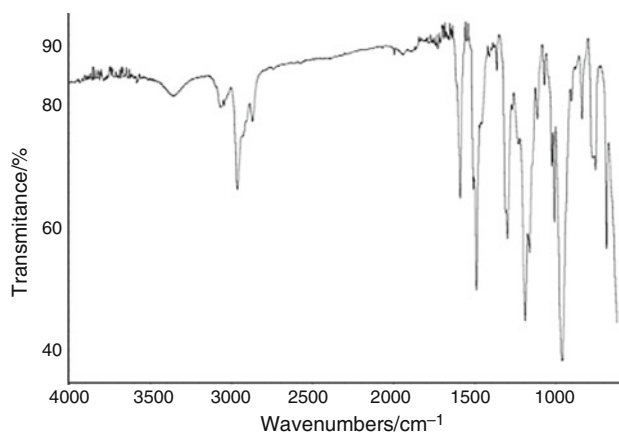
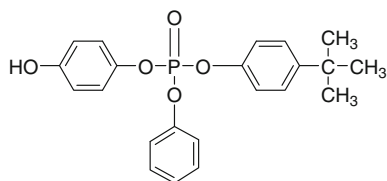


Fig. 12 Infrared spectrum of condensable volatiles from heating of Fyrquel EHC at $250\text{ }^{\circ}\text{C}$ in air

However, it is clear from the phosphorus-31 NMR spectrum of the volatile material (Fig. 13) that it is a mixture of components of the fluid. This spectrum contains peaks at δ -17.7 , -18.0 and -18.3 corresponding to di(*t*-butylphenyl) phenyl phosphate, triphenyl phosphate and diphenyl *t*-butylphenyl phosphate, respectively.

Degradation products, if any, are present in small amounts. The hydroxyl absorption in the infrared spectrum probably reflects the presence of a small amount of phenol

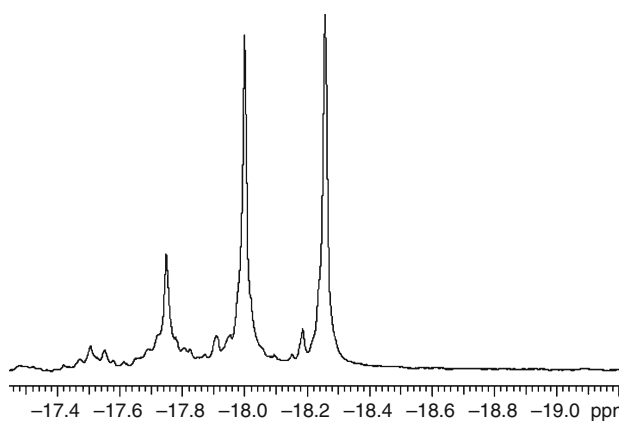


Fig. 13 Phosphorus-31 NMR spectrum of the mixture of volatiles from Fyrquel EHC heated at $250\text{ }^{\circ}\text{C}$

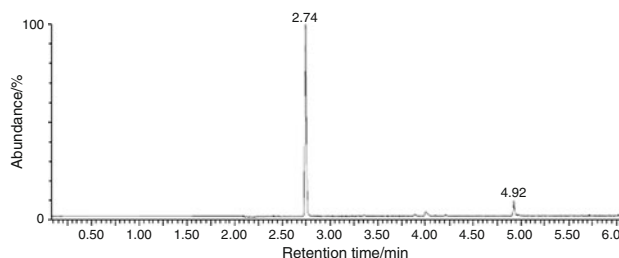


Fig. 14 Gas chromatogram for the mixture of volatiles obtained from heating Fyrquel EHC in air at $175\text{ }^{\circ}\text{C}$

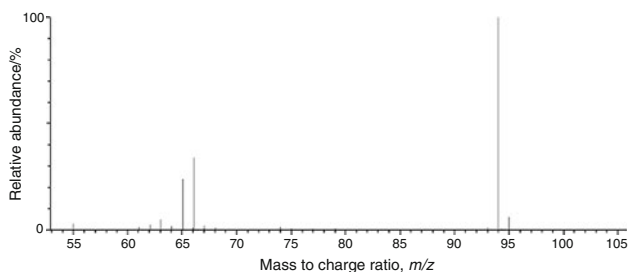


Fig. 15 Mass spectrum of the component of the mixture of the volatiles from Fryquel EHC decomposition at 175 °C in air eluting at 2.74 min (phenol)

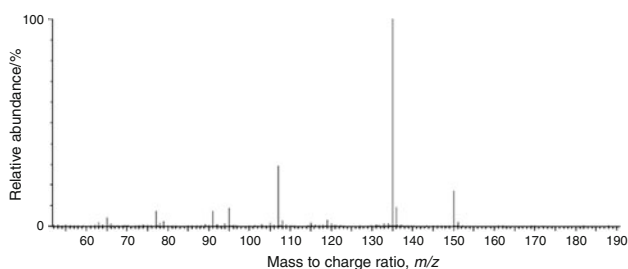


Fig. 16 Mass spectrum of the component of the mixture of the volatiles from Fryquel EHC decomposition at 175 °C in air products eluting at 4.9 min (*t*-butylphenol)

(and/or *t*-butylphenol). At a somewhat lower temperature, 175 °C, components of the fluid are not volatilized. Under these conditions, the fluid does undergo slow degradation—the color of the fluid changes from colorless to yellow to red to black (5 days). A mixture of volatiles collected after 9 days in air at 175 °C contains two components (GC/MS—Fig. 14) identified as phenol (eluted at 2.74 min—Fig. 15) and *t*-butylphenol (eluted at 4.9 min—Fig. 16). The formation of a solid in the fluid, as particulates which can be removed by filtration, is also apparent during this period.

This solid could be collected by filtration. It is insoluble in acetone, methanol, chloroform and dimethyl sulfoxide.

Conclusions

A commercial hydraulic fluid, Fryquel EHC, has been fully characterized using chromatographic, spectroscopic and thermal methods. It is composed of three components of which triphenyl phosphate is primary. Other components are alkylaryl phosphates. This material displays good thermal stability. When subjected to elevated temperatures for extended periods the material slowly degrades to generate volatile phenolic components.

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