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ORIGINAL PAPER

# Reactivity of Triphenyl Phosphorothionate in Lubricant Oil Solution

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**Abstract** Investigating the thermo-oxidative reactivity of anti-wear additives in lubricant oil solution at high temperature can significantly contribute to an understanding of the mechanism of thermal film and tribofilm formation on metal surfaces. In this study, the reactivity of triphenyl phosphorothionate (TPPT) in lubricant oil solution at high temperature (423 and 473 K) has been studied by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. The results show that the TPPT molecule was highly thermally stable and did not completely decompose in oil solution even upon heating at 423 K for 168 h and at 473 K for 72 h. The degradation of the TPPT molecule, which turned out to be a first-order reaction, started taking place after 6 h at both temperatures, leading to the breakage of the P=S bond with the formation of triphenyl phosphate. During these heating experiments, no oil-insoluble compounds were detected. The oxidation of the base oil as a result of the prolonged heating demonstrated that the TPPT molecule did not effectively act as oxidation inhibitor.

**Keywords** Thermo-oxidative degradation · Triphenyl phosphorothionate · Ashless anti-wear additive · Low-SAPS additive · FT-IR · NMR

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## 1 Introduction

Zinc dialkyldithiophosphates (ZnDTPs) have been used as antioxidants, corrosion inhibitors and anti-wear agents in engine oil formulations for decades [1–3]. This class of additives contains a large amount of phosphorus, sulfur and zinc, which can lead to a loss of emission-control catalyst effectiveness and block filters within the exhaust gas after-treatment system [4].

Engine lubricant specifications (e.g. European Automobile Manufacturers' Association ACEA, American Petroleum Institute API, International Lubricant Standardization and Approval Committee ILSAC and Japanese Automotive Standards Organization JASO) are progressively limiting the level of sulfated ash, phosphorus, and sulfur (SAPS) in oil formulations. Several low- or zero-SAPS additives, such as thiophosphates, amine phosphates, metal dithiocarbamates, organometallics and organoboron compounds, have recently been proposed to partially or fully replace ZnDTPs [5].

In contrast to the situation with ZnDTPs, relatively little fundamental research has been carried out with new ashless (i.e. metal-free) additives, such as organosulfur compounds [6], phosphates [6–16], amine phosphates [12], phosphites [11, 17–19], phosphorothionates [12–14, 20–26], and dithiophosphates [12, 21, 22, 24].

Most of the published work deals with films produced by these alternative additives to ZnDTPs under tribological and/or pure thermal conditions. Several analytical techniques have been employed to characterize the reaction layers, such as X-ray photoelectron spectroscopy (XPS) [7, 12, 14, 25, 26], X-ray absorption spectroscopy (XAS) [13, 21–24], X-ray photoelectron emission microscopy (X-PEEM) [24], scanning electron microscopy (SEM) [20, 21], Fourier transform infrared spectroscopy (FT-IR)

[7, 14, 16], Auger electron spectroscopy (AES) [8–10, 14, 17, 18], and atomic force microscopy (AFM) [22].

Najman et al. investigated the thermal films and tribofilms formed by phenyl phosphates on steel [13]. No thermal film formation was detected up to 423 K for triphenyl phosphate, while diphenyl phosphate reacted more easily with steel substrates: in this case the formation of iron(II) polyphosphate was suggested. In the tribofilms formed at 373 K, the data interpretation led the authors to propose the formation of short-chain iron(II) polyphosphate for both additives.

The same authors studied the thermal films produced by triphenyl phosphorothionate (TPPT) at 423 K. Also, in this case, the formation of short-chain iron(II) polyphosphate with a low amount of iron sulfate was suggested [22]. In the tribofilms, short-chain iron(II) polyphosphate, iron sulfides, and sulfates were detected. Increasing sliding time induced an increase in the amount of iron sulfate. After 6 h, comparable amounts of iron sulfate and phosphates were observed. These findings were explained by the authors with a decomposition temperature for triphenyl phosphorothionate of around 423 K. Following the adsorption, the thermal oxidative process took place: after the breakage of the P=S bond, the formation of iron phosphate and sulfate was proposed to occur.

Recently, the reactivity of alkylated TPPTs with air-oxidized steel was investigated in our group [25, 26]. In the absence of mechanical stress, the phosphorothionate molecules adsorbed on the substrate at low temperature (303–353 K), as described by Koyama et al. [27]. The activation temperature for the thermal decomposition of TPPT molecules was found to be around 423 K. The thermal films produced at this temperature consisted of short-chain polyphosphates and oxidized sulfur species, as indicated by the XPS results. The proposed reaction mechanism started with the P=S bond scission, followed by the cleavage of the C–O or P–O bond. The released sulfur was then oxidized to form sulfates.

The thermal films and tribofilms produced on air-oxidized iron surfaces at 373 K in the presence of tributyl thiophosphate were studied by in situ attenuated total reflection (ATR/FT-IR) tribometry, XPS, and temperature programmed reaction spectrometry (TPRS) [14]. Iron polyphosphate and sulfate were detected on the iron surface for both thermal films and tribofilms. After tribological tests, however, the amounts of sulfate and polyphosphate in the films were higher. The presence of sulfur in tributyl thiophosphate was found to favor the formation of long-chain iron polyphosphate and to lower the temperature of chemical and tribochemical reactions by around 50 K compared to the surface reaction of tributyl phosphate [7, 14]. The reaction between TBT and iron was proposed to occur via an initial P=S bond scission to give tributyl phosphite. In accordance

with [3, 8, 11, 17–19], this compound successively produced butoxy groups through P–O bond cleavage.

In contrast with these findings, Sung and Gellman found that the decomposition of tributyl phosphate on iron foil produced butyl intermediates through C–O bond scission [9]. On the other hand, the initial step of the decomposition of tricresyl phosphate, a model compound for aryl phosphates, was the cleavage of the P–O bond with the formation of aryloxy intermediates, independent of the position of the methyl group [10].

While the reactivity of new ashless additives with metal surfaces has been investigated quite extensively, less is known about the thermal degradation of these compounds in oil solution. As was the case for ZnDTPs [1, 3], investigating the reactions that take place in oil solution at high temperature could significantly contribute to elucidating the mechanism of thermal film and tribofilm formation on metal surfaces.

Hilgetag and Teichman have accurately described the chemical behavior of organophosphates and organothio-phosphates, pointing out that the key chemical feature of these compounds is their strong alkylating power [28, 29]. All the chemical reactions could be explained on the basis of Pearson's acid-basis concept [30–32], according to which oxygen is a "hard base" and reacts preferentially with "hard acids," such as protons, "A" metals (alkali metal cations, alkaline earth metal cations, and light transition metal cations in high oxidation states), carbonyl carbon and phosphoryl phosphorus. Sulfur, on the contrary, is a "soft base" and reacts mainly with "soft acids," such as "B" metals (heavy transition metal cations in low oxidation states), tetrahedral carbon, halogens.

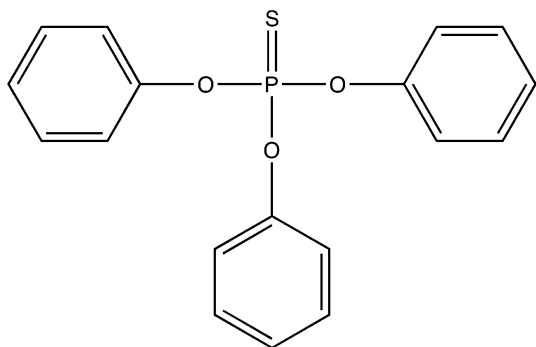
This basic knowledge has been fundamental for understanding the reaction of ZnDTPs in mineral oil at temperatures above 423 K, i.e. the formation of polyphosphates and organic sulfides [1].

In the present work, the thermo-oxidative reaction of TPPT in poly- $\alpha$ -olefin (PAO) has been investigated at 423 and 473 K, which are temperatures typically experienced by automobile engines [33]. A combined investigation using Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy has been carried out for the first time to analyze the oil solutions after the heating experiments.

## 2 Experimental

### 2.1 Materials

Purified TPPT (Irgalube<sup>®</sup> TPPT, Ciba<sup>®</sup> Speciality Chemicals, Basel, Switzerland) (Fig. 1) and commercial poly- $\alpha$ -olefin (PAO, Durasyn<sup>®</sup> 166, Tunap Industrie GmbH & Co.,



**Fig. 1** Chemical formula of triphenyl phosphorothionate

Mississauga, Canada) were used as lubricant additive and base oil, respectively. The purification of TPPT was carried out by liquid chromatography.

For the heating experiments, a  $0.044 \text{ mol dm}^{-3}$  (1.82 wt%) solution of TPPT in PAO was prepared. For dissolving the crystalline TPPT in the base oil, an ultrasonic bath was employed six times for 10 min. The temperature of the lubricant solution was always maintained below 318 K during the ultrasonic bath treatment.

The vacuum filtration of the solutions at the end of the experiments was carried out using cellulose filter papers with a  $2.5\text{-}\mu\text{m}$  particle retention in liquid (Grade 42, Whatman<sup>®</sup>, Maidstone, England).

## 2.2 Methods

### 2.2.1 Heating Experiments

The heating experiments were performed immersing a glass flask ( $40 \text{ cm}^3$ ,  $95 \times 27.5 \text{ mm}^2$ , VWR International, Dietikon, Switzerland) containing  $15 \text{ cm}^3$  of the lubricant solution in a silicone oil bath heated at 423 or 473 K ( $\pm 1 \text{ K}$ ). During the experiment the solution, open to air, was neither stirred nor purged with any gas. The duration of the heating varied between 3 and 168 h at 423 K and between 3 and 72 h at 473 K. The relative humidity was between 22% and 30%.

After the test, the glass flask was removed from the silicone oil bath and left 45 min in air to cool down without any cover. The solution was then vacuum filtered in order to remove all the precipitates.

### 2.2.2 Microelemental Analysis

The microelemental analysis was carried out using a CHN-900 (Leco Corporation, St. Joseph, MI, USA) for carbon and hydrogen, a CHNS-932 (Leco Corporation, St. Joseph, MI, USA) for sulfur and a RO-478 (Leco Corporation, St. Joseph, MI, USA) for oxygen. The phosphorus content was

**Table 1** Transmission FT-IR experimental conditions

Detector	DGTS/KBr
Resolution	$2 \text{ cm}^{-1}$
Number of scans	64
Scan velocity	$0.6329 \text{ cm/s}$
Acquisition time	136 s
Gain control	1

determined by the molybdovanadate method after microwave digestion and leaching ( $2 \times 50 \text{ min}$ ) in concentrated sulfuric acid and perchloric acid at 483–508 K.

### 2.2.3 Fourier Transform Infrared Spectroscopy

Transmission FT-IR spectra were acquired with a Nicolet<sup>™</sup> 5700 Fourier Transform Infrared spectrometer (Thermo Electron Corporation, Madison, WI, USA). The experimental conditions are listed in Table 1. Sampling was performed by placing one drop of solution onto a KBr pellet. The crystalline, purified TPPT was ground with dried KBr and pressed into a pellet.

The spectra were processed with OMNIC<sup>™</sup> software (V7.2, Thermo Electron Corporation, Madison, WI, USA). The single-beam spectrum of the KBr pellet was acquired before each measurement as a background spectrum. Normalization with respect to the methyl asymmetric deformation band, overlapped by the methylene scissor vibration band, of PAO at  $1466 \text{ cm}^{-1}$  [34] and to the C–O–(P) stretching vibration band at  $1183 \text{ cm}^{-1}$  [34] was performed for the lubricant solutions and for the purified TPPT, respectively.

### 2.2.4 Nuclear Magnetic Resonance Spectroscopy

The NMR spectra were recorded in  $\text{CDCl}_3$  (99.8 at.% D, Armar Chemicals, Döttingen, Switzerland) at 300 K using a Bruker Avance 500 NMR spectrometer operating at 500.1 (1-H), 125.8 (13-C), and 202.5 (31-P) MHz. The chemical shifts, given as dimensionless  $\delta$  values, were referred to TMS (1-H and 13-C) and  $\text{H}_3\text{PO}_4$  (85%) following the IUPAC recommendation [35].

## 3 Results

### 3.1 Characterization of Purified TPPT

#### 3.1.1 Microelemental Analysis

The microelemental analysis of TPPT after purification by liquid chromatography is reported in Table 2 together with

**Table 2** Elemental analysis of purified triphenyl phosphorothionate

Element	Concentration (wt%)	
	Measured	Expected
C	63.16 ± 0.07	63.15
H	4.55 ± 0.02	4.42
O	14.1 ± 0.1	14.02
P	9.04 ± 0.05	9.05
S	9.47 ± 0.08	9.37

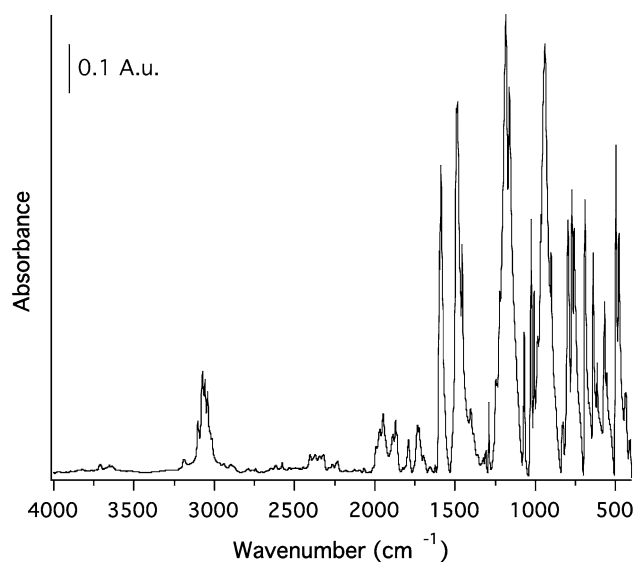
the expected weight percentages. The composition was found to correspond to the molecular formula  $C_{18}H_{15}O_3PS$ .

### 3.1.2 Fourier Transform Infrared Spectroscopy

The transmission FT-IR of TPPT after purification by liquid chromatography (Fig. 2) clearly revealed the characteristic peaks of the TPPT molecule. The IR peaks and the assigned functional groups are listed in Table 3. Three spectral regions could be distinguished:

- the region at high wavenumbers ( $3150\text{--}3000\text{ cm}^{-1}$ )—aromatic CH stretching vibrations;
- the region between  $2100$  and  $1660\text{ cm}^{-1}$ —overtone and combination bands due to the CH out-of-plane deformation vibrations; and
- the fingerprint region ( $1600\text{--}400\text{ cm}^{-1}$ ).

All the reported vibration frequencies are in agreement with the literature [34, 36–39].



**Fig. 2** Transmission FT-IR of purified TPPT. Three spectral regions can be distinguished: (i)  $3150\text{--}3000\text{ cm}^{-1}$ : aromatic CH stretching vibrations, (ii)  $2100\text{--}1660\text{ cm}^{-1}$ : overtone and combination bands due to the CH out-of-plane deformation vibrations, and (iii)  $1600\text{--}400\text{ cm}^{-1}$ : fingerprint region

**Table 3** IR frequencies ( $\text{cm}^{-1}$ ) and functional groups for the transmission FT-IR spectrum of purified TPPT

Frequency ( $\text{cm}^{-1}$ )	Functional group
3102 w, 3095, 3072, 3057, 3040, 3025 s, 3013 w	$\nu\text{CH}$
2067, 1992, 1967, 1947, 1884, 1869, 1790, 1734, 1723, 1696	Overtone and combination bands due to $\gamma\text{CH}$
1598, 1587 s, 1490, 1483 s	$\nu\text{Ph}$
1455	$\omega\text{P-O-Ar}$
1289, 1245, 1221	$\delta\text{CH}$
1183 vs, 1161	$\nu\text{C-O-(P)}$
1074, 1068, 1024	$\delta\text{CH}$
1007	$\nu\text{Ph}$
984 w, 963 w	$\gamma\text{CH}$
940 vs	$\nu\text{P-O-(C)}$
900, 830, 825	$\gamma\text{CH}$
796 m	$\text{P=S (I)}$
771 m, 758	$\nu_s\text{P-O-(C)}$
690	$\gamma\text{CH}$
639 m	$\text{P=S (II)}$
614	$\delta\text{CH}$
573, 568, 555 w	$\delta\text{P-O-Ar}$
497, 479	$\gamma\text{CH}$

$\nu$ : stretching;  $\gamma$ : out-of-plane deformation vibration;  $\delta$ : in-plane deformation vibration;  $\omega$ : wagging

### 3.1.3 Nuclear Magnetic Resonance Spectroscopy

The NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) of TPPT after purification by liquid chromatography are shown in Fig. 3.

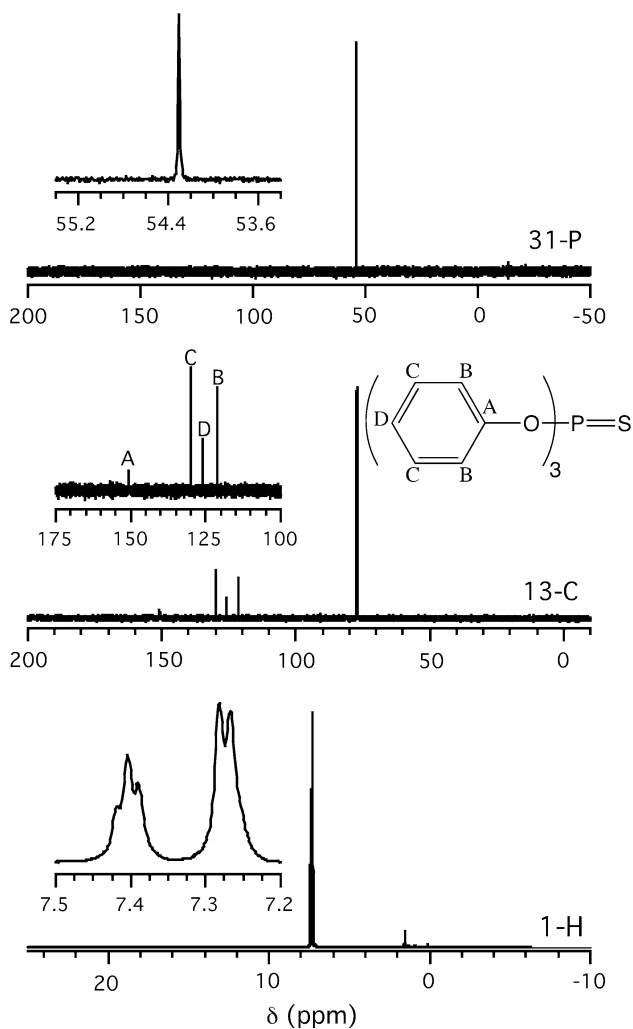
Both the  $^1\text{H}$  and the  $^{13}\text{C}$  spectra showed the characteristic signals of monosubstituted benzene [40, 41]: in the  $^1\text{H}$  spectrum two multiplets are found at 7.40 and 7.28 ppm, whereas in the  $^{13}\text{C}$  spectrum four signals are found in the 120–155 ppm region (150.8, 129.7, 125.7, and 121.3 ppm).

The  $^{31}\text{P}$  spectrum showed a singlet at 54.3 ppm, in agreement with the literature [42–44].

## 3.2 Heating Experiments

During the heating experiments at 423 K, the solutions slowly changed their color, turning yellow-brown after 6–13 h and dark brown after 72–168 h. At 473 K, the color change was faster: the solutions appeared yellow even after 3 h and turned dark brown after 24 h.

After the experiments, all the solutions were vacuum filtered in order to remove all the precipitates. No insoluble compounds were separated out on the filter at either 423 or 473 K.



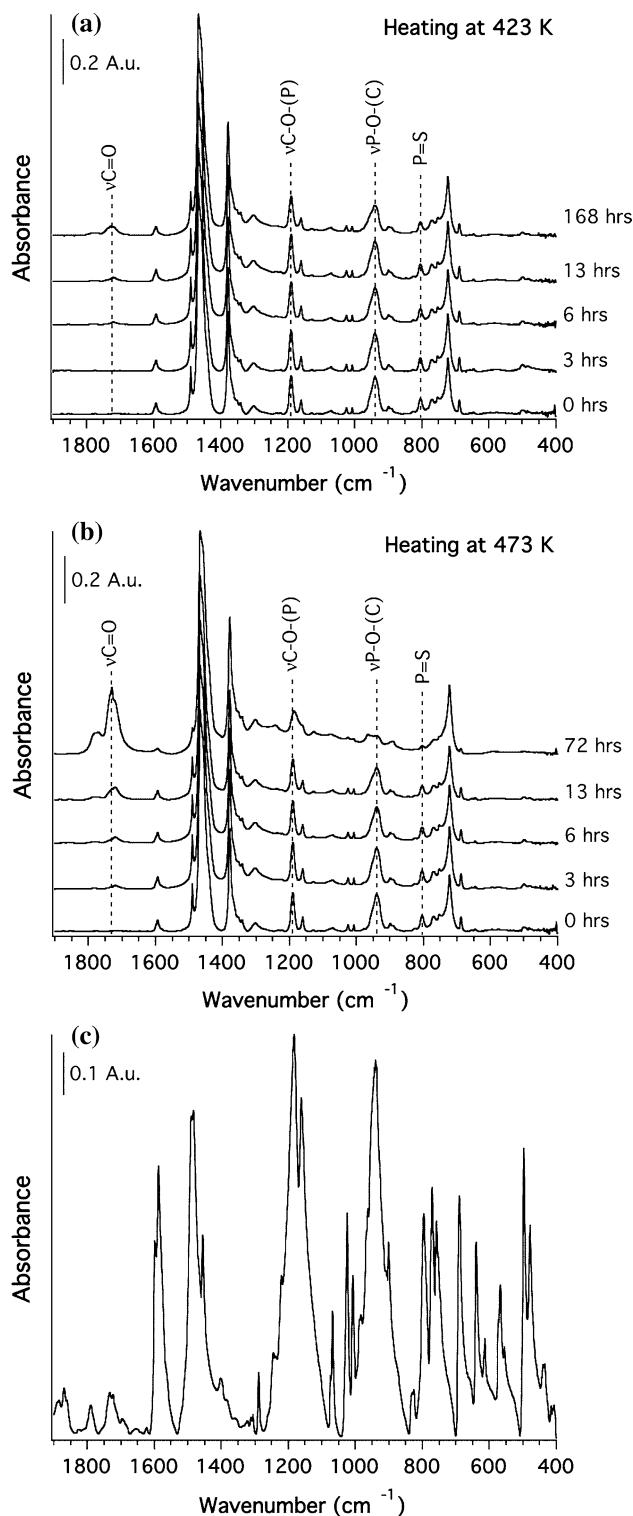
**Fig. 3** NMR spectra (1-H, 13-C, and 31-P) of purified TPPT

### 3.2.1 Fourier Transform Infrared Spectroscopy

**3.2.1.1 Heating at 423 K** The transmission spectra of a  $0.044 \text{ mol dm}^{-3}$  solution of TPPT in PAO heated at 423 K for 3–168 h are reported in Figs. 4a and 5.

The spectrum of the unheated solution (0 h) showed the characteristic IR peaks of the TPPT (Table 3) and PAO ( $1466 \text{ cm}^{-1}$   $\delta_{\text{as}}\text{CH}_3$  and  $\delta\text{CH}_2$ ,  $1378 \text{ cm}^{-1}$   $\delta_{\text{s}}\text{CH}_3$ ,  $890 \text{ cm}^{-1}$   $\rho\text{CH}_3$ ,  $722 \text{ cm}^{-1}$   $\rho\text{CH}_2$ ) [34, 36, 45] molecules. The C–O–(P) stretching ( $1190 \text{ cm}^{-1}$ ) and the P=S(I) ( $803 \text{ cm}^{-1}$ ) vibration bands of TPPT in PAO shifted toward higher wavenumbers with respect to the transmission spectrum of purified TPPT (Table 3).

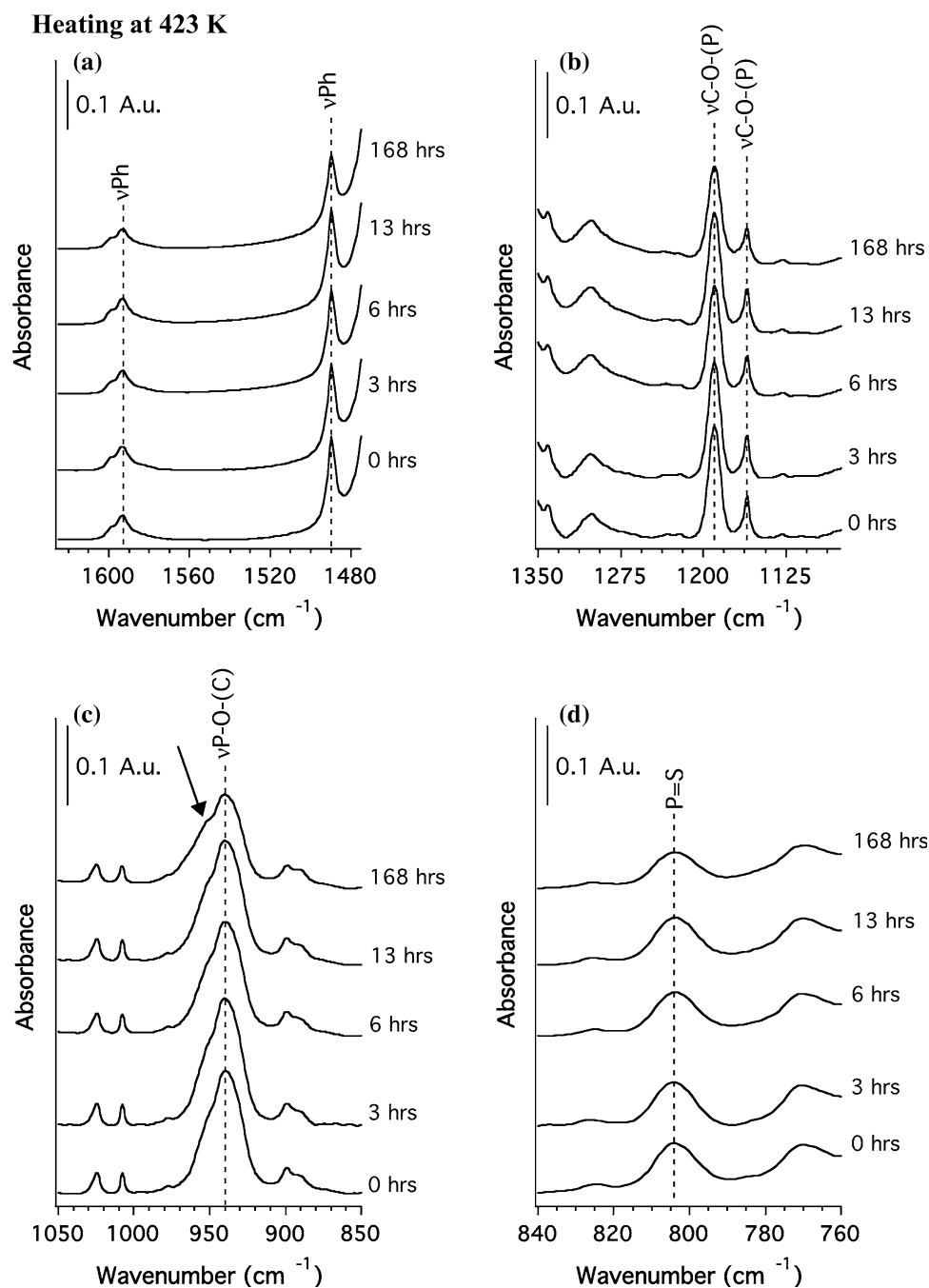
Upon heating at 423 K, no changes in peak position were detected up to 168 h. A slight decrease in peak intensity was observed after 168 h for the  $\nu\text{Ph}$  ( $1593$  and  $1490 \text{ cm}^{-1}$ ),  $\nu\text{C–O–(P)}$  ( $1190 \text{ cm}^{-1}$ ),  $\nu\text{P–O–(C)}$  ( $940 \text{ cm}^{-1}$ ), and P=S ( $803 \text{ cm}^{-1}$ ) vibrations. The band at  $940 \text{ cm}^{-1}$  also exhibited a shoulder at higher wavenumbers after 13–168 h (arrow in Fig. 5c).



**Fig. 4** Transmission FT-IR spectra of a  $0.044 \text{ mol dm}^{-3}$  solution of TPPT in PAO heated at 423 K (a) and 473 K (b) for different times and of purified TPPT (c)

In the  $1550\text{--}1850 \text{ cm}^{-1}$  region, where the C=O stretching vibration is found [34, 45], a new weak and broad peak having a maximum at  $1719 \text{ cm}^{-1}$  was detected

**Fig. 5** Transmission FT-IR spectra of a  $0.044 \text{ mol dm}^{-3}$  solution of TPPT in PAO heated at 423 K for different times



after 13 h (Fig. 4a). After 168 h, this broad absorption band increased in intensity and showed two maxima at 1726 and 1774  $\text{cm}^{-1}$ . Correspondingly, a slight increase of the baseline in the 850–1300  $\text{cm}^{-1}$  region, where the C–O stretching vibration is found [34, 45], was also observed.

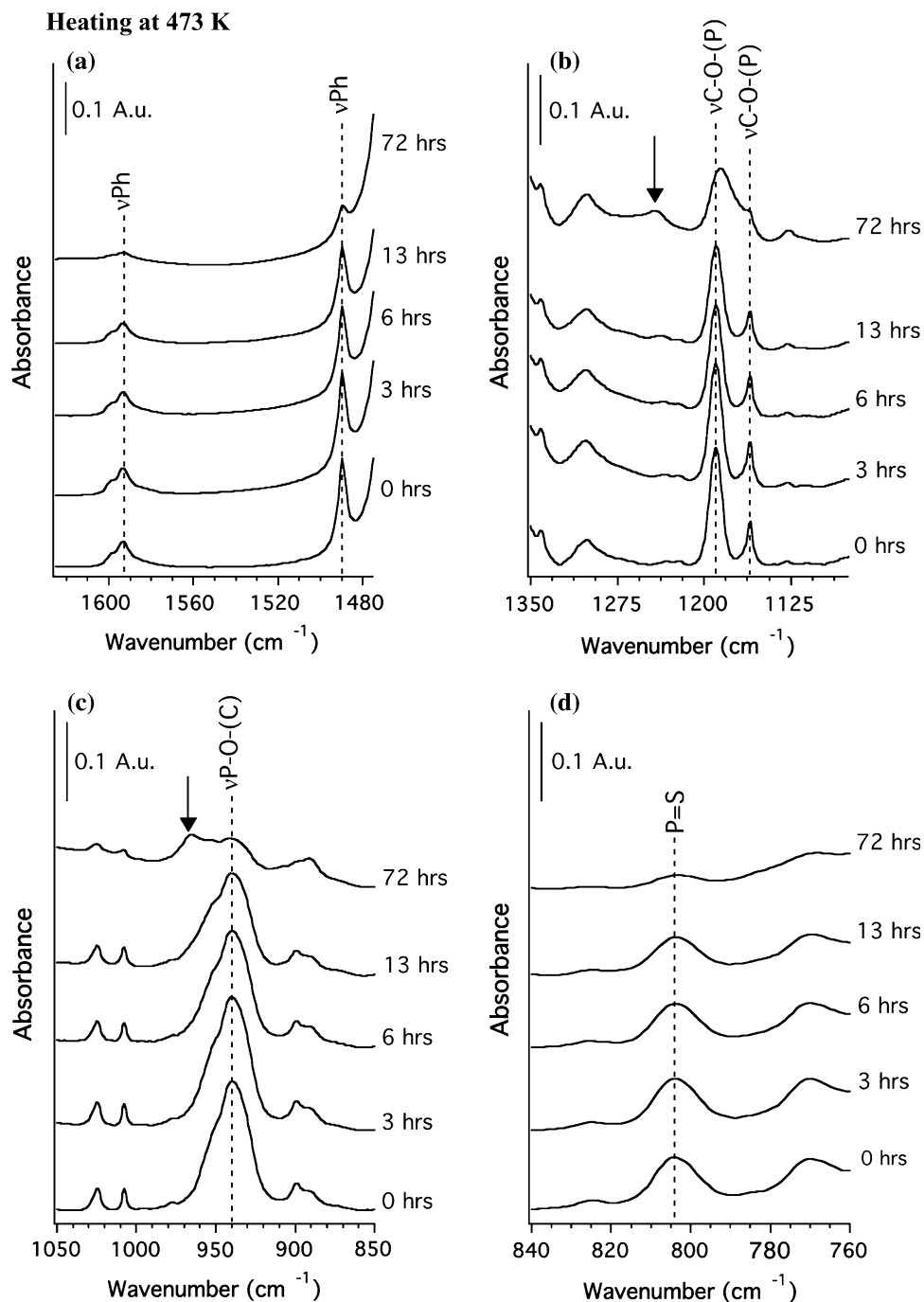
**3.2.1.2 Heating at 473 K** The absorbance of all the characteristic peaks of TPPT ( $\nu\text{Ph}$ ,  $\nu\text{C-O-(P)}$ ,  $\nu\text{P-O-(C)}$ , and  $\text{P=S(I)}$ ) progressively decreased upon heating at 473 K.

A shoulder at higher wavenumbers characterized the  $\nu\text{P-O-(C)}$  absorption band after 13 h and strongly increased after 72 h, when a peak could be clearly observed at 965  $\text{cm}^{-1}$  (arrow in Fig. 6c). A new weak peak at 1243  $\text{cm}^{-1}$  was also detected after 72 h (arrow in Fig. 6b).

The transmission FT-IR spectrum of the solution heated at 473 K for 72 h exhibited a change in shape and a shift to lower wavenumbers (1186  $\text{cm}^{-1}$ ) of the band assigned to the C–O–(P) stretching vibration, when compared to the spectrum of the unheated solution (1190  $\text{cm}^{-1}$ ) (Figs. 4b



**Fig. 6** Transmission FT-IR spectra of a  $0.044 \text{ mol dm}^{-3}$  solution of TPPT in PAO heated at 473 K for different times



and 6b). This might be due to the superposition of the C–O stretching vibration band at ca.  $1175 \text{ cm}^{-1}$  as reported in [46].

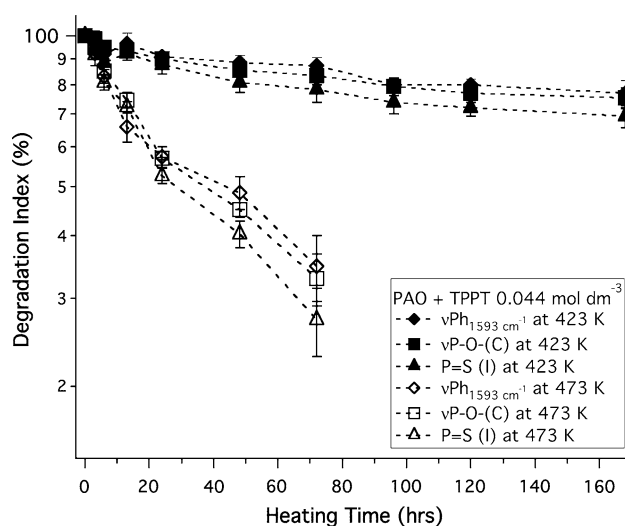
In the  $1550\text{--}1850 \text{ cm}^{-1}$  region, a broad band was already observed after 3 h (Fig. 4b). Besides increasing in intensity, this band had a new small peak at higher wavenumbers (around  $1775 \text{ cm}^{-1}$ ) after 13 h. After 72 h, a very intense absorption band with two maxima at  $1731$  and  $1777 \text{ cm}^{-1}$  could be seen. Correspondingly, an increase of the baseline in the  $850\text{--}1300 \text{ cm}^{-1}$  region, where the C–O stretching vibration is found [34, 45], was also observed.

**3.2.1.3 Degradation Index** In order to investigate the degradation kinetics, the Degradation Index (*DI*) has been defined as:

$$DI = \frac{A_{t,i}}{A_{0,i}} \times 100 \quad (1)$$

where  $A_{t,i}$  is the absorbance of the  $i$ -th vibration at  $t$  heating hours, while  $A_{0,i}$  is the absorbance of the  $i$ -th vibration for the unheated solution.

Figure 7 reports the *DI* of three characteristic vibrations of TPPT ( $\nu\text{Ph}_{1593 \text{ cm}^{-1}}$ ,  $\nu\text{P-O-(C)}$ ,  $\text{P=S(I)}$ ) for a



**Fig. 7** Degradation Index versus heating time at 423 and 473 K for three characteristic vibrations of TPPT in PAO solution

0.044 mol dm<sup>-3</sup> solution of TPPT in PAO as a function of the heating time at 423 and 473 K.

All three absorption bands showed a monotonic decrease of the *DI* values (logarithmic scale on the *DI* axis) as the solutions were heated at both temperatures. Comparing the experiments performed at 423 and at 473 K, an increase in the degradation rate was observed passing from 423 to 473 K. At both temperatures, the *DI* values of the  $\nu\text{Ph}_{1593\text{ cm}^{-1}}$  and  $\nu\text{P-O-(C)}$  bands were always comparable, whereas those of the P=S(I) vibration were slightly lower. The ratio of the *DI* values for the  $\nu\text{Ph}$ ,  $\nu\text{P-O-(C)}$  and P=S(I) absorption bands was  $77 \pm 5 : 75 \pm 4 : 69 \pm 4$  at 423 K and  $35 \pm 5 : 33 \pm 4 : 27 \pm 4$  at 473 K at the end of the experiments, i.e. after, respectively, 168 and 72 h.

As for the characteristic  $\nu\text{C-O-(P)}$  vibration of the TPPT molecule, its *DI* (not shown in Fig. 7) turned out to be always higher than that of the absorption bands considered above ( $\nu\text{Ph}_{1593\text{ cm}^{-1}}$ ,  $\nu\text{P-O-(C)}$ , P=S(I)) as a result of the superposition of the C–O stretching vibration. However, as for the other vibrations of the TPPT molecule ( $\nu\text{Ph}_{1593\text{ cm}^{-1}}$ ,  $\nu\text{P-O-(C)}$ , P=S(I)), a decrease of the *DI* values as the solutions were heated at high temperature and an increase in the degradation rate as the temperature passed from 423 to 473 K was observed for the  $\nu\text{C-O-(P)}$  absorption band.

### 3.2.2 Nuclear Magnetic Resonance Spectroscopy

The NMR spectra (1-H, 13-C, and 31-P) of a 0.044 mol dm<sup>-3</sup> solution of TPPT in PAO heated at 423 and 473 K for, respectively, 168 and 72 h are shown in Fig. 8 together with the spectrum of the unheated solution.

In the case of the unheated solution (0 h), the characteristic peaks of the TPPT molecule were found (see Sect.

3.1.3). The intense peaks between 2 and 0 ppm in the 1-H spectrum and between 60 and 0 ppm in the 13-C spectrum correspond to the aliphatic functional groups of the base oil (PAO) [40, 47].

Upon heating at 423 K for 168 h and at 473 K for 72 h, the characteristic peaks of the TPPT molecule in the 1-H and 13-C spectra progressively decreased in intensity. Moreover, in the former new but weak peaks were found in the 6–2 ppm region, which can be assigned to the hydrogen of a methyl or methylene group bound to a carbonyl or ester group [48]. In the 13-C spectrum no peaks, which can be assigned to these species, can be found because of the small magnetic moment and low natural abundance of carbon-13 [41].

In the 31-P NMR spectrum of the unheated solution (0 h), a narrow peak at 54.4 ppm was found. The dissolution of TPPT in PAO produced a 0.1-ppm downfield shift with respect to the 31-P NMR spectrum of purified TPPT (Fig. 3).

Upon heating at 423 K for 168 h, a new small signal was detected at –16.3 ppm. The singlet at 54.4 ppm was still narrow and intense. Comparing the 31-P NMR spectrum of the solution heated at 423 K for 168 h with that of the solution heated at 473 K for 72 h, an upfield shift of 0.1 ppm was observed for both signals. Moreover, the peak at –16.4 ppm increased in intensity. The integrated intensity ratio of the peaks at 54.4 and –16.3 ppm was 100:18 for the solution heated at 423 K for 168 h and 100:37 for the solution heated at 473 K for 72 h.

## 4 Discussion

### 4.1 Oxidation of the Base Oil

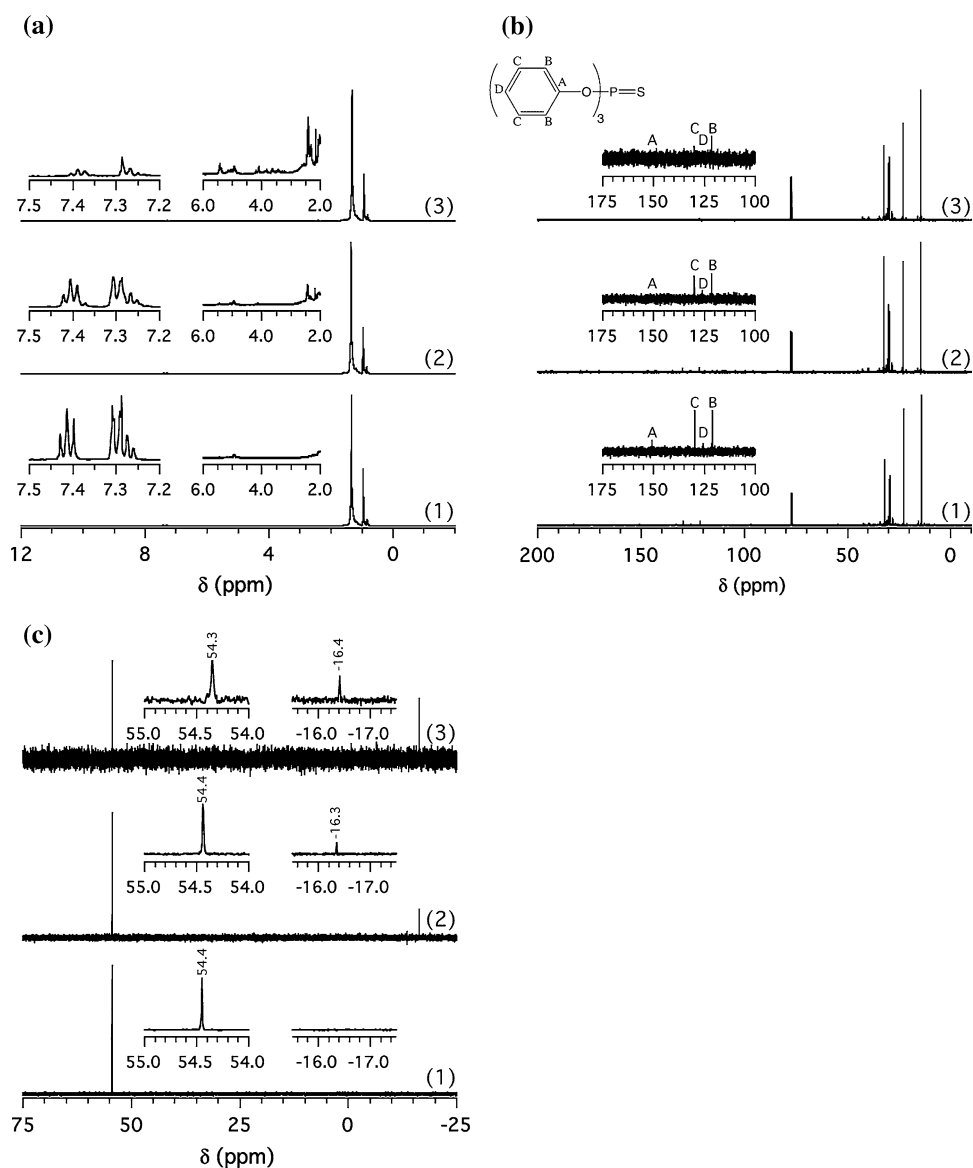
The thermal degradation of lubricant base oils is known to occur at high temperature and to result in the formation of several carbonyl and hydroxy species (lactones, peroxy esters, peroxy acids, esters, ketones, etc.), which are formed by a free radical-initiated chain reaction [33].

FT-IR and NMR spectroscopy have already been used to identify the oxidation products and to investigate the oxidation kinetics [46, 49–54]. The appearance of two broad absorption bands in the 1850–1685 cm<sup>-1</sup> and in the 1300–850 cm<sup>-1</sup> regions of the FT-IR spectrum, corresponding, respectively, to the stretching vibration of the C=O and C–O bonds, has been used to follow the oil-aging process [46, 50, 53]. However, the complex carbonyl envelope made it difficult to give a definitive statement on the chemical nature and distribution of all the species involved [46, 50].

In the present work, the appearance of a broad band in the 1850–1550 cm<sup>-1</sup> region and the increase of the baseline in the 1300–850 cm<sup>-1</sup> region observed in the FT-IR



**Fig. 8** NMR spectra (1-H (a); 13-C (b); 31-P (c)) of 0.044 mol dm<sup>-3</sup> solutions of TPPT in PAO before (1) and after heating at 423 K for 168 h (2) and at 473 K for 72 h (3)



spectra, as well as the presence of new peaks between 6 and 2 ppm in the 1-H spectrum of the TPPT solutions heated at 423 and 473 K, clearly indicate that the base oil (PAO) was getting oxidized during the heating process.

Moreover, the shift of the peak maxima in the 1850–1550 cm<sup>-1</sup> region as the heating time increased, i.e. as the base oil was getting oxidized, could be due to the different distributions of the oxidation products. In the final stages, i.e. after heating at 423 K for 168 h and at 473 K for 72 h, the bands at, respectively, 1774 and 1777 cm<sup>-1</sup> are expected to be mainly from five-membered ring lactones and possibly from small amounts of peroxy esters, whereas the peaks at, respectively, 1726 and 1731 cm<sup>-1</sup> might correspond to ester compounds [46, 50].

Since the solution was not completely depleted of the additive even after heating at 423 K for 168 h and at 473 K

for 72 h (presence of the characteristic TPPT absorption bands in the FT-IR spectra), the TPPT molecule turned out not to be an effective oxidation inhibitor, as opposite to ZnDTPs, which acts as both primary (radical trapping) and secondary (peroxide-decomposing) antioxidants [1, 55].

Control heating experiments on pure PAO (not shown) have also been performed at the same temperatures used in the present work (i.e. 423 and 473 K). The comparison of the FT-IR spectra of pure PAO and solutions of TPPT in PAO heated at the same temperature for the same time showed that the TPPT molecule decreased the oxidation of the base oil (PAO) at 423, but not at 473 K. Moreover, the presence of TPPT in PAO was found to affect the distribution of the species formed during the oil-aging process (shift of the peak maximum in the 1850–1550 cm<sup>-1</sup> region of the FT-IR spectra).

## 4.2 Temperature and Time Effect on TPPT Reactivity in Oil Solution

The transmission FT-IR and NMR spectra presented in this work showed the presence of the characteristic peaks of the TPPT molecule even after heating at 423 K for 168 h and at 473 K for 72 h. During the heating experiments, no oil-insoluble deposit was formed. These findings suggest that the TPPT molecule has a higher thermal stability than ZnDTPs, which are known to completely react in a few hours at high temperature (403–503 K) by a thermo-oxidative degradation route with the formation of a precipitate, whose composition, corresponding to a zinc poly(thio)phosphate compound, resembles that of the surface films obtained in tribological experiments with ZnDTP additives [1, 56–59].

Although the solutions started changing color after 6 h at 423 K and after 3 h at 473 K, the transmission FT-IR spectra exhibited a shoulder at higher wavenumbers (at ca.  $965\text{ cm}^{-1}$ ) in the  $\nu\text{P-O-(C)}$  peak only upon heating at 423 and 473 K for 13 h, indicating the activation of the molecule at these temperatures. Moreover, after heating at 473 K for 72 h a new but weak absorption band at  $1243\text{ cm}^{-1}$ , which can be assigned to the P=O stretching vibration [34], appeared in the FT-IR spectrum. The presence of this band indicates the exchange of the sulfur in the phosphorothionate compound with a phosphoryl oxygen, as reported by Teichman and Hilgetag [29]. The formation of triphenyl phosphate also explains the appearance of a shoulder at higher wavenumbers (at ca.  $965\text{ cm}^{-1}$ ) in the  $\nu\text{P-O-(C)}$  peak [38, 60]. The absence of the P=O stretching vibration band in the FT-IR spectrum of the solution heated at 423 K for 168 h can be due to the increase of the baseline in the  $1300\text{--}850\text{ cm}^{-1}$  region, where the C–O stretching vibration is found [34, 45], induced by the oxidation of the base oil.

These band assignments could be confirmed by the NMR spectra. The  $^{31}\text{P}$  NMR spectra of the solutions heated at 423 K for 168 h and at 473 K for 72 h, in particular, showed the presence of a new peak at, respectively,  $-16.3$  and  $-16.4$  ppm, which corresponds to triphenyl phosphate [42, 44].

The scission of the P=S bond upon heating at 423 and 473 K is also suggested by the *DI* values of the corresponding absorption band in the FT-IR spectra (Fig. 7), which are always slightly lower than the values of the Ph and P–O–(C) stretching vibration peaks. The monotonic decrease of all the *DI* values in Fig. 7, where a logarithmic scale for the vertical axis was used, also suggests that the degradation of the TPPT molecule is a first-order reaction.

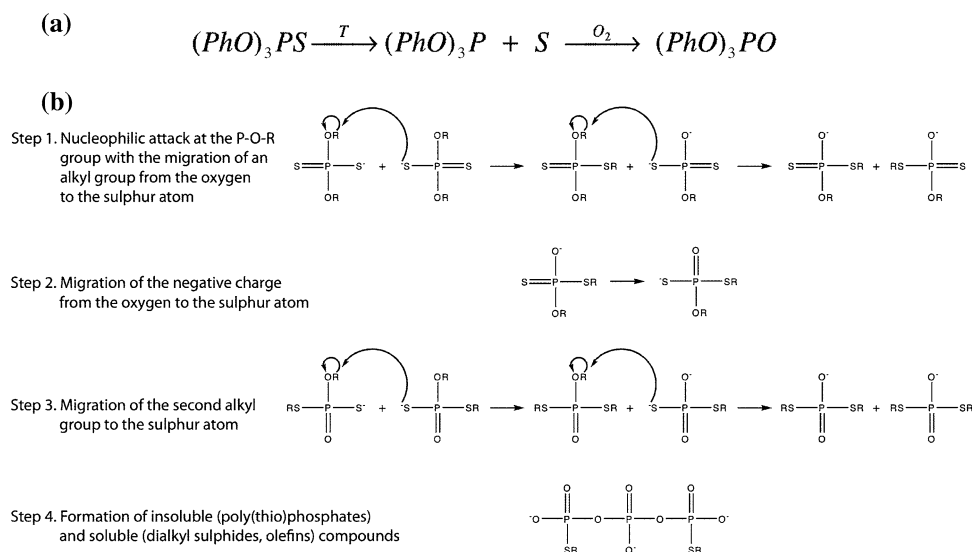
A definitive statement about the reaction step following the P=S bond scission, i.e. the cleavage of the P–O bond to form aryloxy groups or the scission of the C–O bond to give aryl group, cannot be done on the basis of the FT-IR spectra since the superposition of the C–O stretching vibration band of the ester compounds (at ca.  $1175\text{ cm}^{-1}$ ) produced by the oxidation of the base oil with the  $\nu\text{C-O-(P)}$  band results in *DI* values which are not representative of the decrease in absorbance of the latter.

## 4.3 Proposed Reaction Mechanism

Based on the findings mentioned above, the reaction mechanism depicted in Scheme 1a is suggested.

Upon heating at 423 and 473 K for more than 13 h, the TPPT molecule undergoes a nucleophilic attack at the phosphorus atom to cause P=S bond scission to give triphenyl phosphite. Volatile compounds might be also formed during this reaction step. A thermo-oxidative reaction then occurs, which leads to the oxidation of triphenyl phosphite to triphenyl phosphate. No statement can

**Scheme 1** Reaction mechanism in lubricant oil solution of TPPT at 423 and 473 K (a) and of zinc dialkyldithiophosphates at 403–503 K (b)



be made about the following step, i.e. the cleavage of the P–O or C–O bond.

The reaction rate is strongly accelerated as the temperature is increased from 423 to 473 K. However, the TPPT molecule does not completely react in oil solution even upon heating at 423 K for 168 h or at 473 K for 72 h.

It has to be emphasized that the chemical reaction of TPPT might not be the only reason for the decrease in intensity of its characteristic signals in the FT-IR and NMR spectra. The compound volatilization has been addressed as the main reason for the weight loss of triaryl monothio-phosphates during thermogravimetric analyses (TGA) [61]. Although different experimental conditions were employed in this work and this makes it difficult to compare the present results with those reported in [61], some evaporation of the molecule cannot be ruled out as a contributing factor in the decrease in absorbance of the characteristic bands of the TPPT molecule observed in the present study.

The reaction mechanism described above significantly differs from the thermal and thermo-oxidative degradation route of ZnDTPs (Scheme 1b) [1, 56–58]. At temperatures ranging from 403 to 503 K depending on the alkyl groups present, ZnDTPs, being very strong alkylating agents [28–32], undergo a nucleophilic attack at the P–O–R group, which is often followed by an autocatalytic re-alkylation (Step 1 in Scheme 1b). After that, the negative charge migrates from the oxygen to the sulfur atom (Step 2 in Scheme 1b). The second stage of the isomerization reaction can then start resulting in the migration of the alkyl groups from the oxygen to the sulfur atom (Step 3 in Scheme 1b). Subsequent reactions lead to the formation of insoluble (poly(thio)phosphates) and soluble (diaklyl sulfides, and olefins) compounds (Step 4 in Scheme 1b).

Aromatic esters, having no tetrahedral carbon bound to oxygen, cannot undergo dearylation by the same  $S_N2$ -type process (i.e. reaction initiated by a nucleophilic attack on the  $\alpha$ -carbon of the alkyl group) [58] and this results in a higher thermal stability than alkyl thiophosphate esters [33].

## 5 Conclusions

The following conclusions can be drawn from the results presented in this work:

- (i) Upon heating solutions of TPPT in PAO at 423 and 473 K, the base oil (PAO) gets oxidized, indicating that the TPPT molecule is not an effective oxidation inhibitor;
- (ii) The TPPT molecule, being not completely decomposed upon heating at 423 K for 168 h and at 473 K for 72 h, has a high thermal stability in lubricant oil solution;

- (iii) The thermo-oxidative reaction of TPPT in lubricant oil solution starts with the scission of the P=S bond, leading to the formation of triphenyl phosphite;
- (iv) The reaction rate is strongly accelerated as the temperature is increased from 423 to 473 K;
- (v) No oil-insoluble compounds are formed during the heating experiments.

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