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^{31}P NMR ANALYSIS OF THERMAL DECOMPOSITION OF TRIBUTYLMETHYL-PHOSPHONIUM DIMETHYLPHOSPHATE

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Abstract

Zinc dialkyldithiophosphates (ZDDPs) are widely used anti-wear oil additives that have been shown to reduce the conversion efficiencies of catalytic converters in automobiles and to harm the environment in general. Ionic liquids (ILs) are one type of alternative anti-wear additives that have been widely researched in recent years. Among the ILs of interest is tributylmethylphosphonium dimethylphosphate (PP), which has been found to have superior friction-reducing properties as compared to ZDDP under some conditions. We have heated ZDDP and PP samples for various lengths of time to temperatures up to 200 ˚C. The thermal degradations have been compared by utilizing ^{31}P nuclear magnetic resonance techniques. The results suggest that PP may perform better as a friction-modifier than ZDDP in some situations involving high temperatures.

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Introduction

Zinc dialkyldithiophosphates (ZDDPs) are anti-wear additives that have been used in commercial motor oils for decades. However, in recent years, studies have shown that ZDDPs can break down and that phosphorus oxides, sulfur oxides, and ash deposits can harm catalytic converters in automobiles, reducing their conversion efficiencies[1,2]. Furthermore, ZDDPs often decompose to poisonous sulfur- and phosphorus-containing compounds, which can pollute soil and groundwater[3]. In addition, the performance of ZDDP as an anti-wear additive has been shown to be poor at high temperatures. A study by Fuller *et al.*[4] found that, after heating an oil solution containing ZDDP for 1 hour at 200 ˚C, no oil-soluble phosphorus-containing species remained in the solution. Fuller *et al.* also noted that the oil solution had anti-wear properties that were inferior to base oil alone after it had been heated for 1 hour at 200 ˚C[4]. As a result of these limitations, attention has been drawn to alternative anti-wear additives, such as ionic liquids (ILs).

ILs are organic salts composed of a cation (typically containing phosphorus or nitrogen) and a weakly coordinating anion. By changing the cation and anion compositions, the structures of ILs can be tuned to optimize their physical and chemical properties for specific tasks[5,6]. This makes ILs promising candidates for use as lubricants in extreme environments (high temperatures, ultra-low pressures, etc.), where conventional oils and lubricants fail[7]. In addition to being environmentally-friendly (due to low volatility), ILs exhibit several characteristics that are desirable in lubricant additives including low melting points, low vapor pressure, non-flammability, high thermal conductivity, and thermal stability[5,8]. Furthermore, the results of a recent study[9] suggest that phosphonium-based ILs may be less detrimental to catalytic converters than ZDDPs.

Totolin *et al.*[10] studied the anti-wear performance and friction-reducing properties of imidazolium borane ILs and found that the addition of a phosphate-based IL, tributylmethylphosphonium dimethylphosphate (PP), significantly improved the tribological properties of the ILs. X-ray photoelectron spectroscopy analysis of wear scars confirmed the presence of phosphate-based tribofilms, which significantly improved the tribological properties of ILs when PP was included as an additive.

More recently, Arshad *et al.* compared the anti-wear properties of several ILs to those of ZDDP[11]. Results of experiments performed at 100 ˚C involving applied forces ranging from 2 N to 10 N suggest that PP exhibits a significantly lower coefficient of friction than ZDDP. The results of the experiments performed by Arshad *et al.* (involving glycerol, glycerol with PP, and glycerol with ZDDP) are summarized in Table 1[12].

Given these encouraging results, additional information about the thermal and tribological properties of PP is needed. The goal of the experiments described in this paper was to study the thermal decomposition of PP using ^{31}P nuclear magnetic resonance (^{31}P NMR) and to compare the results to those of ZDDP as a reference. While the thermal decomposition of ZDDP has been studied previously[4,13] using ^{31}P NMR, the authors are unaware of any study in which the degradation of PP has been studied via ^{31}P NMR.

Experimental Methods

The ZDDP samples used in the experiments described here were in the form of commercially-available REV-X Zinc Oil Additive (~50% ZDDP by volume[14]). The PP samples used were obtained from Ambeed (USA) and each had a nominal purity of 97%. Each sample was prepared by pouring 2.00 ± 0.01 g of the additive into a glass vial, which was then submerged in sand (to ensure uniform heating) on a hot plate that had been preheated to the desired

Table 1. Summary of the results of experiments performed by Arshad et al. [11] involving glycerol (G), glycerol with tributylmethylphosphonium dimethylphosphate (G + PP), and glycerol with zinc dialkyldithiophosphate (G + ZDDP).

Applied Load	Coefficients of Friction		
	G	G + PP	G + ZDDP
2 N	0.1000 ± 0.0005	0.1000 ± 0.0001	0.1050 ± 0.0001
5 N	0.0457 ± 0.0007	0.0430 ± 0.0001	0.0570 ± 0.0001
10 N	0.0400 ± 0.0020	0.0240 ± 0.0005	0.0290 ± 0.0014

temperature. The temperature and time intervals for heating were chosen to match the ones used by Fuller *et al.*[4] for comparison. Ten samples containing PP and ZDDP were divided into five groups: an unheated group, a group heated at 100 ˚C for 48 hours, a group heated at 150 ˚C for 6 hours, a group heated at 150 ˚C for 24 hours, and a group heated at 200 ˚C for 1 hour.

Afterwards, approximately 0.275 g from each of the five ZDDP samples and approximately 0.128 g from each of the five PP samples were pipetted into separate 4 mL vials. Then 700 µL of chloroform-d ($CDCl_3$) was added to each of the PP samples and 600 µL of $CDCl_3$ was added to each of the ZDDP samples to act as a solvent for ^{31}P NMR analysis. The internal standards, triphenylphosphine oxide and tributylphosphate, were added to the NMR samples of ZDDP and PP, respectively. Then 750 µL of the mixture from each sample was pipetted into NMR tubes and ^{31}P NMR analysis was conducted on each one. The data was analyzed using Mnova software. The chemical shifts of the NMR spectra were normalized using the internal standards.

Results and Discussion

Figures 1 and 2 are ^{31}P NMR spectra for five samples of the ZDDP additive and five samples of PP (heated at various temperatures for different time intervals), respectively. In Figure 1, all spectra were normalized using the intensity of the peak located at approximately 104 ppm, and in Figure 2 all spectra were normalized using the intensity of the peak located at approximately 32 ppm.

ZDDP does not exist as a single molecule, but as a group of multiple molecules that contain phosphorus. The peaks shown in the ZDDP spectra with higher chemical shifts (~102-110 ppm) are due to more basic forms of ZDDP, while the peaks with lower chemical shifts (~93-102 ppm) are due to more neutral forms of ZDDP. There do not appear to be any significant differences in the ^{31}P NMR spectra shown in Figure 1 for the unheated ZDDP sample, the sample heated at 100 ˚C for 48 hours, and the sample heated at 150 ˚C for 24 hours. However, the spectrum for the sample heated at 150 ˚C for 6 hours does suggest some thermal decomposition. The reason for evidence of decomposition in the spectrum for the sample heated at 150 ˚C for 6 hours, but not in the spectrum for the sample heated at the same temperature for 24 hours, is not understood. It is possible that the anomaly is the result of contamination. However, in general, the results shown in Figure 1 are consistent with the results of a previous study of the thermal decomposition of ZDDP using ^{31}P NMR[4], which found that no detectable amounts of ZDDPs or ZDDP decomposition intermediates were present after oil samples containing ZDDP were heated at 200 ˚C for 1 hour[4]. The results of wear tests performed by Fuller *et al.* also suggested that anti-wear films derived from ZDDP samples heated at 200 ˚C for 1 hour performed poorly even compared to anti-wear films containing base oil alone (with no additives present)[4].

As mentioned previously, PP exists as two ionic molecules, one with a phosphorus atom present in a phosphate group and the other with a phosphorus atom present in a phosphine group. Thus, the phosphorus atoms have different oxidation states, and this corresponds to ^{31}P NMR signals at two different chemical shifts, as shown in the spectra in Figure 2. Analysis performed using Mnova software indicates that the ratios of the peak intensities in the PP spectra remain essentially unchanged (approximately 4:3) as the samples were heated to temperatures up to 200 ˚C. The absence of any other peaks in the NMR spectra and the consistent peak intensity ratios indicate that no appreciable thermal degradation occurred for the PP samples. This result suggests that PP may provide consistent friction-reducing properties and anti-wear properties at temperatures up to 200 ˚C.

Conclusions

A comparison of the ^{31}P NMR results for ZDDP and PP shown here suggest that ZDDP completely degrades when heated at a temperature of 200 ˚C for 1 hour, while PP does not. The results shown in Figure 1 indicate that ZDDP may begin to degrade at temperatures as low as 150 ˚C, while the results shown in Figure 2 show no significant thermal decomposition of PP as it is heated

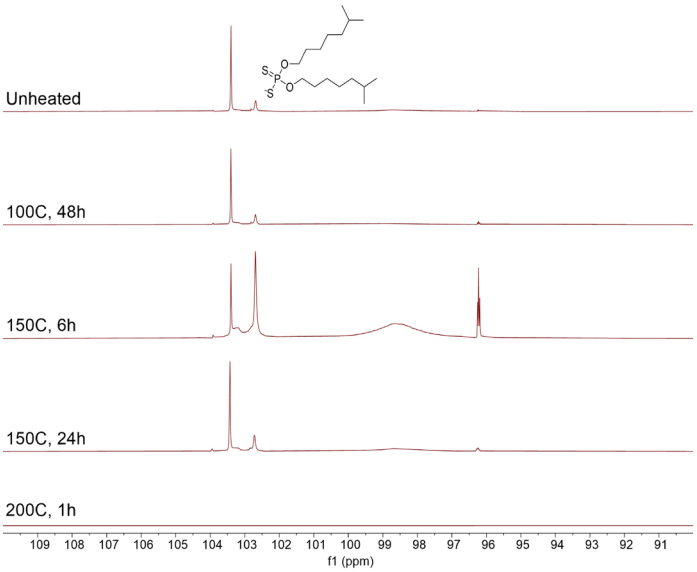

Figure 1. ^{31}P NMR spectra for zinc dialkyldithiophosphate (ZDDP) additive samples that (from top to bottom) were unheated, heated at 100 ˚C for 48 hours, heated at 150 ˚C for 6 hours, heated at 150 ˚C for 24 hours, and heated at 200 ˚C for 1 hour.

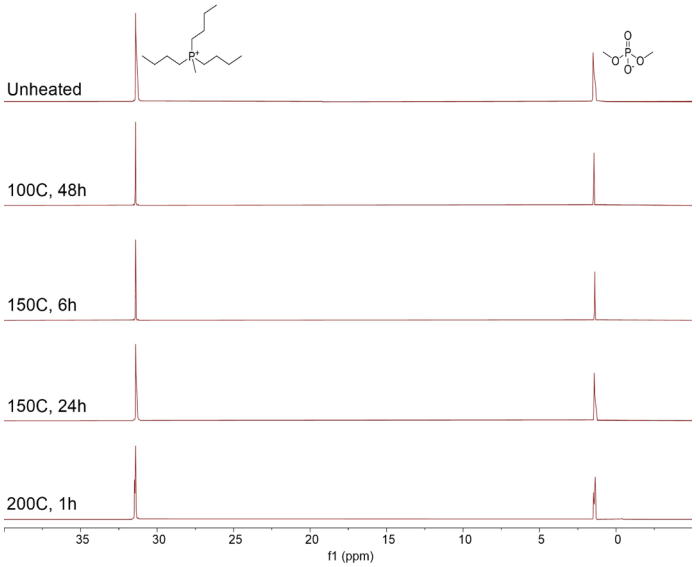

Figure 2. ^{31}P NMR spectra for tributylmethylphosphonium dimethylphosphate (PP) samples that (from top to bottom) were unheated, heated at 100 ˚C for 48 hours, heated at 150 ˚C for 6 hours, heated at 150 ˚C for 24 hours, and heated at 200 ˚C for 1 hour.

to temperatures up to 200 ˚C. When considered in the context of the experimental results of Fuller *et al.*[4] and Arshad *et al.*[11], the results indicate that PP may perform better as a friction-modifying and anti-wear additive than ZDDP in some situations involving temperatures in the range of 100 ˚C to 200 ˚C.

In the future, additional experiments should be conducted in order to more thoroughly compare the friction-reducing and anti-wear properties of ZDDP and PP, and further studies should be performed to gain information about any detrimental effects that PP could possibly have on catalytic converters and the environment in general. Furthermore, additional experiments in which a shearing force is acting on the lubricants at various temperatures for different time intervals should also be performed in order to better understand the tribological properties of PP.

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