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FTIR Study of the Reaction of Polyphosphoric Acid and Model Bitumen Sulfur Compounds

J-F. Masson^{*1} and P. Collins²

Abstract

Bitumen is a complex mixture of alkanes, cyclo-alkanes, aromatic and substituted fused aromatics that contain a number of heteroatomic functional groups. To improve its properties, bitumen is often modified with an additive that may or may not be reactive. Polyphosphoric acid (PPA) is a reactive additive used to increase the viscosity of bitumen in summer temperatures. Given the complexity of bitumen, the nature of its reaction with PPA is in many respects unclear. To better understand the reactions between bitumen and polyphosphoric acid, we have used Fourier transform infrared spectroscopy and thinlayer chromatography to study the reaction of model bitumen sulfur compounds. We have used saturated, aromatic and oxidized sulfides, the most common forms of sulfur in bitumen. Only the oxidized sulfide, the sulfoxide group, was found to react upon heating with PPA. This work concludes with a comparison of the relative reactivity of PPA with model functional groups that contain nitrogen, oxygen, and sulfur, and its incidence on the possible reactivity of oxidized and unoxidized bitumens with PPA.

Keywords: Asphalt, bitumen, polyphosphoric acid, model, heteroatoms, reaction, sulfur, tetrahydrothiophene, benzothiophene, thianaphthene, tetramethylene sulfoxide.

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Introduction

The reaction between bitumen and polyphosphoric acid (PPA) is of great technological interest. Lately, PPA-modified bitumen has been used in significant volumes in roadway construction to increase bitumen viscosity and reduce its deformation in summer temperatures under repeated traffic load.¹ The PPA-induced chemical reaction(s) that lead to the increase in bitumen viscosity have been the subject of some work,²⁻⁴ but the complexity of bitumen composition does not lend itself easily to the investigation of detailed chemical reactions. Consequently, we have used bitumen model compounds to investigate the possible reactions between bitumen and PPA. In this respect, we have previously studied models with organic functional groups that contain nitrogen^{5,6} and oxygen.^{5,7} Here, we report on the reaction of model bitumen sulfur compounds.

In the study of PPA-modified bitumen by gel permeation chromatography and atomic force microscopy, a reduction in molecular weight and a change in bitumen morphology is observed.^{2,3} Given that sulfur is the most abundant heteroatom in bitumen, found mostly as aliphatic and aromatic sulfides,^{8,9} it was hypothesized² that sulfides might be the subject of a nucleophilic substitution that would help to explain the reduction in bitumen molecular weight upon its treatment with PPA (Figure 1).

To verify the claim of a possible nucleophilic displacement reaction of sulfur compounds in bitumen, we reacted PPA with model compounds that contained sulfur functional groups (Figure 2). Tetrahydrothiophene is typical of sulfides found in the saturated portion of bitumen, whereas the aromatic benzothiophene and thianaphthene are typical of structures found in heavier fractions, the resins and asphaltenes.⁸⁻¹⁰ Given that bitumen sulfides are known to oxidize upon the aging of bitumen to produce sulfoxide

groups,^{8,9,11} the reactivity of PPA with the sulfoxide analog of thianaphthene, i.e., tetramethylene sulfoxide, was also investigated. Fourier-transform infrared spectroscopy (FTIR) and thin-layer chromatography (TLC) were used in the investigation.

Experimental

Materials. The bitumen model compounds (Figure 2) were purchased from Sigma-Aldrich. Except for tetramethylene sulfoxide (TMSO), their purity was 99% or better and they were used as received. TMSO was 96% pure and it contained water as evidenced from its infrared spectrum, which revealed water absorptions at 3440 and 1660 cm⁻¹. TMSO was dried over MgSO₄ (10% w/w) for three days and distilled before being used. PPA, 83.3 % P₂O₅, or stated otherwise 115% H₃PO₄ equivalent,⁴ was provided by ICL Performance Product LP.

The model compounds were heated individually with PPA at 150 °C for 1 h under an argon blanket. The PPA/reactant weight ratio was 1:5. Details were provided before.⁵ The reaction of the model compounds with PPA was followed by TLC and FTIR. Plates of silica gel on flexible aluminium backing were used for TLC, with the starting compound and the reaction products, if any, being eluted with various solvents, including for instance, heptane, toluene, ethyl acetate, methanol, and their mixtures. A UV lamp (365 nm) or a spray solution of alkaline potassium permanganate¹² was used to reveal the compounds on the TLC plates.

After heating the PPA-model mixture and in cases where TLC showed a new product, PPA was removed from the mixture by washing with an aqueous alkali solution. The product was back extracted in toluene before the solvent was evaporated with a rotary evaporator, leaving a liquid product for later analysis. In efforts to determine the nature and the extent of the reaction of the model compound with PPA, the infrared spectrum of each model compound was compared to the spectrum of the product retrieved after heating with PPA, if any. In this respect, fifty scans were acquired between $400 \text{ and } 4000 \text{ cm}^{-1}$ as indicated earlier in greater detail.⁵

Results and Discussion

A nucleophilic displacement on sulfides, as illustrated in Figure 1, would lead to a phosphorylated product and a thiol, with respective O–P=O and S–H groups. These groups would readily be identified by FTIR, although the thiol function gives a weak signal,¹³ and TLC would help to determine the number of new products, if any.

Upon the heating of the saturated tetrahydrothiophene (THT) with PPA, the sulfide was found to be immune to the effect of PPA as no trace of a new compound could be found on TLC plates and no new FTIR absorbances could be detected. It was surmised that the protonated intermediate (in brackets in Figure 1) required stabilization of its charge and that an aromatic sulfide might provide such stabilization by means of resonance on an aromatic ring, as we have seen before with other model bitumen compounds.⁵⁻⁷ Consequently, PPA was heated separately with the aromatic benzothiophene and thianaphthene. Given the reaction of PPA with indole,⁶ the nitrogen analog of thianaphthene, a condensation reaction of two thianaphthene through the double bonds was expected. Surprisingly, however, neither FTIR nor TLC revealed any reaction of the aromatic sulfides in conditions typical of those used to prepare PPA-modified bitumen. It was therefore concluded that the original postulate² illustrated in Figure 1 was invalid. Nucleophilic displacement in sulfides cannot explain the decrease in bitumen molecular weight.

Upon the aging of bitumen, some sulfides oxidize to sulfoxides.¹⁴ As the reaction of carbonyl groups is catalyzed by PPA,⁷ a reaction of the sulfoxide group was also

expected. Consequently, TMSO was heated with PPA and it was found to have reacted. In the absence of PPA, however, TMSO remained unaffected by heating at 150°C.

TMSO heated with PPA gave a liquid whose TLC analysis showed the almost complete reaction of TMSO into a major new compound and two minor ones, as revealed with an alkaline $KMnO_4$ spray (Figure 3). Prior to the reagent spray, TMSO and the minor products were fluorescent under UV-light exposure, but THT and the major product were not, which confirmed their aliphatic nature. As our interest was to assess the extent of the reactivity of the sulfoxide group, the major compound was not purified and its structure was not ascertained. Notwithstanding, the FTIR spectrum of the mixture was quite revealing. Figure 4 shows its spectrum as Rx, along with those of TMSO, PPA and THT for comparison. Consistent with the TLC results, was a 98% loss of the sulfoxide infrared absorbance from TMSO at 1022 cm⁻¹. From infrared frequency compilations,¹³ the functional groups in the major reaction product were also identified. A comparison of Rx with THT revealed a C–S band of nearly equal intensity at 686 cm⁻¹ and common CH₂ absorbances at 1440, 1255, and 958 cm⁻¹. Two weak absorbances at 3057 and 3017 cm⁻¹ for =C-H stretch were consistent with a C=C stretch at 813 cm⁻¹, whose position indicated possible tri-substitution. A typical aldehyde absorbance at 2718 cm^{-1} was consistent with a C=O absorbance at 1723 cm^{-1} from an aliphatic aldehyde. The loss of the ring deformation bands between 400 and 800 cm⁻¹ (top of Figure 4) also demonstrated the opening of the TMSO ring during the reaction. An open ring with an aldehyde at one end was consistent with the absence of methyl absorbances in Rx between 2800 and 3000 cm⁻¹ and near 1376 cm⁻¹. Finally, the breadth of the methylene band near 1200 cm⁻¹ and the trio of bands near 1600 cm⁻¹ alluded to the presence of phosphate groups from PPA, but the absence of a correspondingly strong PO–H stretch near 500 cm^{-1} made improbable the presence of a phosphate group in the major product.

With FTIR alone the reaction course or the exact nature of the major product of the reaction between TMSO and PPA could not be determined, but two reaction courses can be pondered, namely, the thermal degradation and the condensation of the sulfoxide group. Upon heating, aliphatic sulfoxides can eliminate sulfur oxide to produce an alkene.^{15,16} The heating of TMSO without PPA, however, did not reduce the sulfoxide absorbance visible at 1022 cm⁻¹ in Figure 4. Its loss upon heating with PPA first suggested a catalytic effect from PPA, but the retention of sulfur and oxygen in the reaction product, as visible from new C=O and C–S bands indicated that another reaction course likely prevailed. In this respect, a cascading condensation of sulfoxide groups, similar to that of carbonyl groups,^{7,17} may better explain the double bond in Rx. Obviously, further work would be required to determine more precisely the nature of the major reaction product, but for this investigation, it was sufficient and clear that the sulfoxide group was very reactive in conditions used to prepare PPA-modified bitumen.

With the completion of this work on model sulfur compounds, we have explored the reactivity of bitumen functional groups with bitumen heteroatoms, nitrogen,^{5,6} oxygen,^{5,7} and sulfur. The relative reactivity of these groups in conditions typical of those used to prepare PPA-modified bitumen can then be compared (Table 1). From the relative reactivity of the various groups and their concentrations in bitumen, predictions of bitumen reactivity with PPA can be made. In this respect, two issues are noteworthy. Firstly, oxidized groups, namely the carbonyl and the sulfoxide groups, are fairly reactive, which suggest that the reactivity of oxidized bitumens might be quite different from that of unoxidized ones. On first thought, the reactivity of oxidized bitumens might be expected to exceed that of unoxidized bitumens, but if oxidation eliminated reaction sites for PPA, then the reactivity of bitumen would be reduced. Clearly, further work will be required to make valid predictions of the reactivity of oxidized bitumen with PPA. Secondly, with Table 1 and the known organic functional groups concentrations tabulated by Jones for several unoxidized bitumens,¹⁸ attempts to predict the reactivity of bitumen with PPA were fairly successful.¹⁹

Conclusion

PPA is used to enhance bitumen properties. Given the complexity of bitumen, the nature of the reaction between the two materials is best described based on work with model bitumen compounds. Here the reaction of models with a sulfur functional group was investigated. The findings indicated that sulfide groups, be they aliphatic or aromatic in character, remain inert when heated with PPA at 150 °C for 1 h. These findings invalidated the postulate that nucleophilic displacement of sulfides lead to a decrease in bitumen molecular weight. In contrast to sulfides, the sulfoxide group was found to be very reactive. Given that sulfoxide groups are found in fairly high concentrations in blown bitumens, these findings suggest that oxidized and unoxidized bitumen would not be equally reactive towards PPA.

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References

(1) Orange G, Martin J.; Menapace A.; Hemsley M.; Baumgardner G. Rutting and moisture resistance of asphalt mixtures containing polymer and polyphoshoric acid modified bitumen. *Road Mater. Pavement Design* **2004**, *5*, 325–354.

(2) Baumgardner, G. L.; Masson, J-F.; Hardee, J. R.; Menapace, A, M.; Williams, A.
G. Polyphosphoric acid modified asphalt: Proposed mechanisms. *Proc. Assoc. Asphalt Paving Technol.* 2005, *74*, 283–305.

(3) Orange, G.; Dupuis, D.; Martin, J.-V.; Farcas, F.; Such, C.; Marcant, B.
Chemical modification of bitumen through PPA: Properties–microstructure relationship.
Proceedings of the 3rd Euraphalt and Eurobitume Congress, Vienna, Austria, 2004; paper 334, book 1, 733–745.

(4) Masson, J-F. Brief review of the chemistry of polyphosphoric acid (PPA) and bitumen. *Energy Fuels* **2008**, *22*, 2637–2640.

(5) Masson, J-F.; Gagné, M. Ionic pairs in polyphosphoric acid (PPA)-modified bitumen: Insights from model compounds. *Energy Fuels* **2008**, *22*, 3390–3394.

(6) Masson J-F.; Gagné, M. Polyphosphoric acid (PPA)-modified bitumen:Disruption of the asphaltenes network based on the reaction of non-basic nitrogen withPPA. *Energy Fuels* 2008, 22, 3402–3406.

(7) Masson J-F.; Gagné, M.; Robertson, G.; Collins, P. Reactions of polyphosphoric acid and bitumen model compounds with oxygenated functional groups. *Energy Fuels*, accepted for publication, doi 10.1021/ef800511v.

(8) Green, J. B.; Yu, S. K.-T.; Pearson, C. D.; Reynolds, J.W. Analysis of sulfur compound types in asphalt. *Energy Fuels* **1993**, *7*, 119–126.

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(9) Mitra-Kirtley, S.; Mullins, O. C.; Ralston, C. Y.; Sellis, D.; Pareis, C.

Determination of sulfur species in asphaltenes, resin and oil fractions of crude oils. *Appl. Spectros.* **1998**, *52*, 1522–1525.

(10) Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: NY, 1999.

(11) Lamontagne, J.; Dumas, P.; Mouillet, V.; Kister, J. Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: Application to road bitumens. *Fuel* **2001**, *80*, 483–488.

(12) Jork, H.; Funk, F.; Fischer, W.; Wimmer, H. *Thin-Layer Chromatography: Reagents and Detection Methods;* VCH Publishers: Weinheim, 1990.

(13) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: San Diego, CA, 1991.

(14) Gotte, V.; Rogalev, A.; Goulon, J.; Goulon-Ginet, C.; Michon, L.; Guilard, R.;
Martin, D. A study using sulfur K-Edge XAS of bitumens, asphaltenes, maltenes and
their oxidation products by comparison with model compounds. *J. Phys. IV France* 1997,
7, C2,667–C2,668.

(15) Ternay, Jr., A. L. *Contemporary Organic Chemistry*; W. B. Saunders Company:Philadelphia, PA, 1979, p.1056.

(16) Herrington, P. R. Thermal decomposition of asphalt sulfoxides. *Fuel* 1995, 74, 1232–1235.

(17) Roeske, R. W.; Bright, D. B.; Johnson, R. L.; DeJarlais, W. J.; Bush, R. W.; Snyder, H. R. Polyphosphoric acid as a reagent in organic chemistry. X. Two yellow hydrocarbons from acetophenone. *J. Am. Chem. Soc.* **1960**, *82*, 3128–3133. (18) Jones, IV., D. R. Materials reference library for asphalt cements: A concise data compilation. Report SHRP-A-645, Strategic Highway Research Program, National Research Council, Washington, D. C., 1993;

http://onlinepubs.trb.org/Onlinepubs/shrp/SHRP-A-645.pdf (accessed September 24, 2008).

(19) Masson, J-F.; Collins, P.; Woods, J. R.; Bundalo-Perc, S.; Margeson, J. Chemistry and effects of polyphosphoric acid on the microstructure, molecular mass, and glass transition temperatures of asphalts. *J. Assoc. Asphalt Paving Technol.*, submitted for publication, and for presentation at the 2009 annual meeting.

reactivity	model	function	reaction type	ref.
high	weak base	pyridine	ionic pair	5
high	amphoteric	quinolone	ionic pair	5
high	weak acid	alkyl-phenol	dealkylation,	7
			phosphorylation	
high	oxidized group	sulfoxide	condensation	this work
medium	weak acid	pyrrole	bridging, phosphorylation	6
medium	oxidized group	ketone	condensation	7
low	medium acid	carboxylic	bridging	7
		acid		
low	weak	ether	bridging	7
	amphoteric			
none	weak	sulfide	none	this work
	amphoteric			

Table 1. Relative Reactivity of Bitumen Model Compounds with PPA^a

^a PPA with a 115% relative content of H_3PO_4 .



Figure 1. Hypothetical nucleophilic displacement in aliphatic (R) or aromatic (Ar) sulfides upon the action of PPA, whose anion is written PPAO⁻.



Figure 2. Bitumen model compounds with sulfur. Clockwise from the top left, tetrahydrothiophene, benzothiophene, thianaphthene, and tetramethylene sulfoxide.



Figure 3. TLC results from TMSO, THT, and the products of the reaction between TMSO and PPA (Rx) as obtained from nine min of elution in toluene. The solvent front is shown by the dotted line, and the numbers show the Rf values. The compounds were detected with an alkaline KMnO₄ spray reagent.



Figure 4. FTIR spectra of TMSO and PPA at the top, and THT and the products of the reaction between TMSO and PPA (Rx) at the bottom. The very strong S=O band at 1022 cm⁻¹ in TMSO, whose peak is along the dotted line at 0.79 absorbance units, was truncated for a better appreciation of the bands of lesser intensity. For the same reason, the right and left figures are scaled differently. Except for PPA, the intensity of the spectra was normalized at the CH₂ peak near 2945 cm⁻¹.